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UNIVERSITY.... OF ALBERTA

DEGREE FOR WHICH THESIS WAS PRESENTED.... Ph. D.

YEAR THIS DEGREE GRANTED.... 1973

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ELECTRODE POTENTIALS OF IRON, COBALT, NICKEL AND HYDROGEN IN A NEAR-EUTECTIC KCl - NaCl - $AlCl_3$ MELT

by

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A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE

OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

EDMONTON, ALBERTA

FALL, 1973

THE UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled "Electrode Potentials of Iron, Cobalt, Nickel, and Hydrogen in a Near-Eutectic KCl - NaCl - $AlCl_3$ Melt" submitted by Martin Skala in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry.

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ABSTRACT

Standard potentials of the Fe(II)/Fe(O), Co(II)/Co(O), Ni(II)/Ni(O), and H(I)/H_2(g) electrochemical couples in a near-eutectic KCl-NaCl-$AlCl_3$ melt were determined by direct measurements of equilibrium potentials of metal electrodes and the hydrogen electrode (H_2 on polished Pt) at concentrations between 0.1 and 1 mol% of the metal (II) or hydrogen (I) compounds.

Voltammetric waves recorded with a platinum microelectrode showed a slight irreversibility of the redox systems of iron, cobalt and nickel; this, together with the corrosive action of hydrogen compounds present in the melt, may explain the differences of 0.04 to 0.10 V between the measured deposition and equilibrium potentials of ferrous metals in this molten system.

Hydrogen compounds, probably HCl, are shown to cause the corrosion of iron, cobalt and nickel. Their concentration in the melt can easily be lowered to approximately 0.1 mol% by reduction with aluminum metal or by electrolysis. It is, however, not always possible to reduce their concentration below this level, probably because of slow equilibria that exist between them and other, oxygen-containing or organic, impurities in the melt. The remaining HCl may account for the residual corrosion of iron which was observed even in the presence of aluminum metal.

ACKNOWLEDGEMENTS

The author wishes to express his thanks to Dr. James A. Plambeck for continuous guidance and encouragement.

During the experimental work, helpful discussions were held with Drs. Kenneth F. Denning and Dominique-Louis Piron.

The author is grateful to the Department of Chemistry of this University for teaching assistantships, to the National Research Council of Canada for support through an Operating Grant, and to the Defence Research Board of Canada for support under Grant 5412-09.

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CHAPTER I

INTRODUCTION

A. FUSED CHLOROALUMINATES

Molten salt systems containing aluminum trichloride, referred to as chloroaluminate melts, have been studied for decades. At first this was in conjunction with the electrometallurgy of aluminum. Later, practical interest shifted towards using these melts as electrolytes in fuel cells. The electrochemical properties of haloaluminates have therefore been studied more often and more thoroughly than other properties of these substances. One particular approach, used by Yntema and co-workers [49,82-84,86] consisted in determining the deposition potentials of various metals in these melts. This was followed by studies of standard electrode potentials of some metals by Plambeck and co-workers [1,2,31,32,64]. It is probable that assembling such data and comparing them with results obtained in other liquid systems will contribute to a more accurate physicochemical knowledge of haloaluminate melts and help to prepare a basis for their industrial exploitation.

Although various chloroaluminate melts, of binary, ternary and more complex composition, have been studied, one can divide them into two groups according to their content of aluminum chloride [30]. This is the main factor

influencing their behavior. Differences between sodium- and potassium-containing melts with one and the same percentage of aluminum chloride are only of secondary importance. One type of melts can be described as consisting mainly of fused tetrachloroaluminates, $MAlCl_4$. They result from the melting of mixtures with approximately 50 mol% $AlCl_3$ and according to various authors [15,67,81] their main components are M^+ and $AlCl_4^-$ ions. The particular melt in this group which has been studied most extensively has the stoichiometric composition $NaAlCl_4$, or $NaCl:AlCl_3$. The other group is represented by melts with a high content of aluminum chloride, typically between 60 and 66 mol% $AlCl_3$. They are often designated as eutectic melts, because binary and ternary eutectics frequently appear within this region of the respective phase diagram. Most measurements in this group were done in the $KCl-NaCl-AlCl_3$ eutectic melts, whose formal composition is given as 66 mol% $AlCl_3$, 20 mol% NaCl and 14 mol% KCl by Wasilewski et al. [85], 63.5 mol% $AlCl_3$, 20.0 mol% NaCl and 16.5 mol% KCl by Plotnikov and Shvartsman [66], and as 62.1 mol% $AlCl_3$, 25.1 mol% NaCl and 12.8 mol% KCl by Treadwell and Terebesi [80].

The electrochemical studies of Yntema and co-workers and of Plambeck, Hames and Anders refer to the $KCl-NaCl-AlCl_3$ eutectic, usually accepting the composition specified in Wasilewski's paper [85], which corresponds to the stoichiometry $MCl:2\ AlCl_3$. In the density and melting-point

studies of Midorikawa [52,53] the composition of the eutectic is given as 60 mol% $AlCl_3$, 26 mol% NaCl and 14 mol% KCl. This melt was also used by Martin de Fremont and co-workers [50]. Recently some electrochemical work has been done in melts with an intermediate aluminum chloride content [34,35]. Attempts were made by Torsi and Mamantov [77], by Fannin, King and Seegmiller [18,19] and by Boxall, Jones and Osteryoung [9] to describe continuous changes in the chemical equilibria and the electrochemical properties of chloroaluminate melts due to their varying aluminum chloride content.

The experimental work in this thesis was performed in a melt containing 64 mol% $AlCl_3$, 22 mol% NaCl and 14 mol% KCl, a composition very close to that of the ternary eutectic and slightly on the MCl side of the ideal MCl:2 $AlCl_3$ composition. Other chloroaluminate melts will therefore only be discussed when comparisons appear to help in the interpretation of experimental results. In some cases, physical constants not known for the exact melt composition under study will be estimated from data known for other similar compositions. There is less need for such a procedure today than in earlier molten salt research, but rejecting it completely would impose unnecessary limitations on the interpretation of experimental results. Some chemical problems, in particular those of acid-base equilibria in chloroaluminate melts [77,81] were first studied for melts

with close to 50 mol% $AlCl_3$. The results of such studies will be summarized briefly prior to their application to the ternary near-eutectic melt used in this thesis.

The physical constants of the KCl-NaCl-$AlCl_3$ eutectic are summarized by Hames [31]. Midorikawa [52] found its melting point to be 93°C and this value is now widely accepted, Wasilewski's [85] lower value of 70°C being attributed to supercooling. At the temperature of our measurements, 135°C, the melt density for a composition of 65 mol% $AlCl_3$, 25 mol% NaCl and 10 mol% KCl is 1.7 (Midorikawa [53] and its specific conductivity approximately 0.3 $ohm^{-1}cm^{-1}$ [54]. The useful range of potentials is 2.06 V [1], the cathodic limit being the deposition of aluminum and the anodic one the evolution of chlorine.

Metal chlorides and oxides are generally found to be soluble in the KCl-NaCl-$AlCl_3$ eutectic [82,83]. Lower oxidation states of some elements are found to be stabilized in melts with a high aluminum chloride content [1,31], but not necessarily in other chloroaluminate melts [9]. Reasons for this stabilization are discussed by Hames [31] and Anders [1]. While steric factors, charge densities of anions and even lattice energies might be involved, the Lewis-acid character of aluminum trichloride seems to be the main cause of this effect [9]. The higher the formal charge of a metal cation, the more its stability would depend on proper coordination, in this case coordination with chloride

ions, which have the role of electron donors, i.e., of a Lewis base. According to Fannin, King and Seegmiller, the actual concentration of chloride ions in a NaCl:2 $AlCl_3$ melt is low, of the order of 10^{-6} mol% [19].

B. CHEMICAL EQUILIBRIA IN CHLOROALUMINATE MELTS

As mentioned earlier in this introduction, Trémillon and Letisse [81] have successfully described chloroaluminate melts with close to 50 mol% $AlCl_3$ in terms of acid-base equilibria between various ionized species. "Acidity" here is to be understood in its broadest sense, as defined by Lewis [71]: acids are acceptors of electron pairs, bases donors of electron pairs. In chloroaluminate melts, whenever a chloride ion combines with an aluminum-containing species, an aluminum-chlorine bond is formed with the electron pair for this bond being donated by the chloride ion. This makes the chloride ion a base within a Lewis-type acid-base system in a chloroaluminate melt. Trémillon and Letisse [81] then define acids as acceptors of Cl^- ions and bases as either Cl^- ions themselves or donors of Cl^-. A base is tied to its conjugate acid by an equation of the form

$$\text{base} = \text{acid} + Cl^-$$

which can be considered an analogy of the classical Brønsted definition

$$\text{(base) } B + H^+ = BH^+ \text{ (acid)}$$

and an even closer analogy of acid-base equilibria in oxygen containing melts, where according to Lux [47] and Flood [23]

the donation of electron pairs proceeds as a donation of the oxide ion, O^{2-}, so that we can write [10] e.g., for molten hydroxides

$$\text{(base)}\ 2\ OH^- = H_2O\ \text{(acid)} + O^{2-}$$

and for molten nitrates [17]

$$NO_3^- = NO_2^+ + O^{2-}.$$

The ideally neutral (50 mol%) $NaCl-AlCl_3$ melt can be viewed as molten sodium tetrachloroaluminate, $NaAlCl_4$, primarily existing in the form of sodium cations and $AlCl_4^-$ anions. To a slight extent, there is dissociation:

$$2\ AlCl_4^- = Al_2Cl_7^- + Cl^-.$$

The dissociation constant, with concentrations in mole fraction units, is

$$K = X_{(Al_2Cl_7^-)} * X_{Cl^-} / X^2_{AlCl_4^-}$$

Its numerical value is independent of the concentration units used [77]. Boxall, Jones and Osteryoung [9] give a list of K values at 175°C (see first column of Table I). If the extent of this dissociation is small and consequently $X_{AlCl_4^-}$ remains constant, a value analogous to the ionic products of slightly ionized solvents can be defined as follows:

$$K_S' = X_{(Al_2Cl_7^-)} * X_{Cl^-}$$

or

$$K_S = [Al_2Cl_7^-] * [Cl^-]$$

Table I

Apparent Dissociation Constants K and "Ionic Products" K_S Equimolar $NaCl:AlCl_3$ Melt at 175°C

$K \times 10^8$	pK_S (K_S in mol^2/kg^2)	Reference and Authors
13.3±1.5	5.48±0.05	[81] Trémillon, Letisse
8.0±1.8	5.69±0.06	[77] Torsi, Mamantov
7.77		[18] Fannin, King, Seegmiller
10.6±0.2	5.56±0.01	[9] Boxall, Jones, Osteryoung

The values of K are given in reference [9].
The first pK_S value is given by Trémillon and Letisse [81], the other two are calculated from the K value.

on the molality scale used in [81]. Its numerical value was determined at 175°C by Trémillon and Letisse [81]:

$$K_S = (3.4 \pm 0.4) \times 10^{-6} \text{ mol}^2/\text{kg}^2.$$

Numerical values of $pK_S = -\log K_S$ are listed in the second column of Table I.

This dissociation of the tetrachloroaluminate anion is a formal analogy of dissociation processes known to occur in various other solvents. Contrary to most other cases, dissociation here generates two anions and no cation. This, however, does not rule out the application of Lewis' general theory of acids and bases. An electron pair goes hand in hand with the Cl^- ion and acids and bases in molten sodium tetrachloroaluminate are therefore quite properly defined as, respectively, acceptors and donors of Cl^- ions. This then makes $pCl = -\log X_{Cl^-}$ a correct characteristic of the acidity or basicity of any particular chloroaluminate melt. The formal analogy with pH in aqueous systems follows directly from the definitions of "acid" and "base" as given above. Low pCl indicates a high concentration of chloride ions and thereby a basic melt. In practice, the lowest pCl that can be reached will often be that of a saturated solution of MCl in $MAlCl_4$ at the given temperature. Trémillon and Letisse [81] found it to be 1.31 ± 0.02 at 175°C with M = Na; on our mole fraction scale that would be $pCl = 2.02 \pm 0.02$.

An acidic melt, or one with a high pCl, is rich in species that are acceptors of electron pairs. From the point of view of formal composition we speak about $AlCl_3$-rich melts, although the actual acidic species, in the Lewis sense, is the heptachlorodialuminate (III) anion, $Al_2Cl_7^-$. Even systems with substantially more than 50 mol% $AlCl_3$ as far as their formal composition is concerned, can be successfully described in terms of pCl, although this may be found less practical when the concentration of the Lewis acid $Al_2Cl_7^-$ approaches that of its conjugate base $AlCl_4^-$ because here one enters a "buffer" region of nearly constant pCl. This was duly recognized by Leroy in his thesis, as quoted in [50] and [81]. A quantitative treatment of the buffer system, however, proves to be complicated, because several aluminum-containing species are present, as pointed out by Mamantov and co-workers [77,79]. The following actual concentrations of various species can be read from a graph in the paper by Fannin, King and Seegmiller [18]:

Species	Approximate Composition	
	63 mol% $AlCl_3$	67 mol% $AlCl_3$
$X_{AlCl_4^-}$	0.2	0.12
$X_{Al_2Cl_7^-}$	0.2	0.25
$X_{Al_2Cl_6}$	0.04	0.12
X_{Cl^-}	2×10^{-8}	10^{-8}
$X_{AlCl_3(monomer)}$	5×10^{-5}	7×10^{-5}

Boxall, Jones and Osteryoung [9] improved this set of data achieving better agreement with the experimentally determined electomotive forces of concentration cells by introducing an activity coefficient ($\neq 1$) for $AlCl_4^-$.

As we progress from equimolar $MCl:AlCl_3$ or $MAlCl_4$ melts towards $AlCl_3$-rich ones, it is no longer justified to regard the tetrachloroaluminate ion as the main solvent particle, virtually neutral in the acid-base sense, with only a formal role of the conjugate base to $Al_2Cl_7^-$. In a melt with more than 50 mol% $AlCl_3$, the tetrachloroaluminate ion acquires a distinctly basic character, being able to donate chloride ions to any suitable acceptor. The equilibium [9]

$$\underset{\text{base}}{2\ AlCl_4^-} = \underset{\text{acid}}{Al_2Cl_7^-} + Cl^-$$

is still valid, although in $AlCl_3$-rich melts it does not correspond any more to the "pure solvent" dissociation discussed by Trémillon and Letisse [81]. According to Boxall, Jones and Osteryoung [9], two other equilibria must be taken into consideration if the presence of Al_2Cl_6 and $AlCl_3$(monomer) in the melt is to be accounted for. The authors chose

$$2\ AlCl_3 = Al_2Cl_6 \quad \text{and} \quad AlCl_4^- + AlCl_3 = Al_2Cl_7^-.$$

Small amounts of $Al_3Cl_{10}^-$ are also present in $AlCl_3$-rich chloroaluminate melts at equilibrium, but within the range of melt compositions mentioned in this thesis, they are not important in determining the position of chemical equilibria

[9].

In spite of this complexity of the solvent system, changes in the concentration of chloride ions, following additions of acidic or basic compounds, are uniform and very small in melts with approximately 55 mol% or more $AlCl_3$. So are the changes in observed equilibrium potentials of aluminum electrodes in these melts [9,18,19], which are related to the activity of chloride ions through the Nernst equation. Osteryoung and co-workers [9] mention as an example that after an addition of 100 mg $AlCl_3$ per gram of a NaCl:2 $AlCl_3$ melt, the potential of an aluminum electrode in this melt would only increase by 25 mV. This finding is especially important when mutual comparisons of data obtained in slightly different melt compositions are attempted.

The tendency of $AlCl_3$-rich melts, such as the KCl-NaCl-$AlCl_3$ ternary eutectic, to maintain a constant Cl^- concentration also is of prime importance when the hydrogen redox system is studied: in equimolar melts Trémillon and Letisse [46] found that the oxidized form of the H(I)/H_2 couple was HCl, which would generate chloride ions upon reduction:

$$HCl + e^- = 1/2\ H_2 + Cl^-$$

With the melt buffer system acting as a trap for chloride ions one might expect the reduction of HCl to be favored thermodynamically by acidic (high-pCl) melts. On the other hand, the scarcity of chloride ions might provoke some

dissociation of HCl and give some stability to free (i.e in some way solvated) hydrogen ions. This might lead to effects which did not exist or were not significant in the equimolar NaCl:$AlCl_3$ melt studied by Trémillon and Letisse [46,81].

C. MELT CONTAMINATION AND PURIFICATION

According to Boston [8] there are three main types of impurities that are likely to be present in a chloroaluminate melt. These are:

1. heavy metal compounds
2. organic impurities
3. products of melt hydrolysis.

Heavy metal compounds (mostly those of iron), cause no difficulties. They are usually eliminated from commercial aluminum chloride during its sublimation in the presence of finely divided aluminum metal [1,8,35]. Small residual amounts of heavy metals are easily precipitated from the melt itself by metallic aluminum. Voltammetric checks, reported in this thesis, confirm the successful elimination of iron compounds. Once a purified melt is prepared and placed in an inert (typically glass) container inside a dry box, there is little probability of any re-contamination by heavy metals.

Organic impurities pose much more serious problems [8]. They can be present in commercial reagents or they can penetrate into the melt during various operations, e.g., by

back diffusion from oil pumps. Aluminum chloride and all "acidic" chloroaluminate melts react with a number of organic compounds [13], usually with the formation of a carbonium cation and a tetrahaloaluminate anion:

$$R.CH_2Cl + Al_2Cl_7^- = (R.CH_2^+ \; . \; AlCl_4^-) + AlCl_4^-$$

Bailey and Prest [3] used $NaCl-AlCl_3$ molten mixtures to catalyze halogen exchange or elimination reactions, the mechanism of which involves carbonium ions. A reaction between an organic halide and an "acidic" melt is basically a donation of the electron-rich chloride ion: it is an acid-base reaction in the Lewis sense. It is favored by the presence of strong electron-pair acceptors in $AlCl_3$-rich melts and is therefore difficult to prevent.

The products of reactions between organic compounds and the melt are generally very stable [22,38] and chemical methods have proved "surprisingly ineffective" [8] in attempts to remove them from the melt. Trémillon and Letisse [46] were able to get and maintain a water-clear (and therefore presumably free from organics) equimolar $NaCl:AlCl_3$ melt merely by contact with metallic aluminum. For $AlCl_3$-richer melts Torsi and Mamantov [77] specify digesting of the melt with pieces of aluminum wire in a sealed quartz tube at 300°C for several days. In another paper [78], the same authors preferred to circumvent the "in-melt" purification step by using pure aluminum chloride synthesized from aluminum and hydrogen chloride according

to Bjerrum, Boston and Smith [5].

The need for elimination of organic impurities from the melt was probably first felt by authors who studied the optical properties of fused chloroaluminates. Munday and Corbett [59] as well as Morrey [56] explained the brown coloration of most $AlCl_3$-containing melts by the presence of organic compounds. This seems to be generally accepted [8] although occasionally other reasons for the coloration are given [21].

Workers dealing with the electrochemical properties of the molten system were less concerned about the color of their melts; they usually reported it [50], sometimes stating that it did not interfere with measurements. In fact it is quite possible that the organic compounds present in the melt do not interfere directly with electrochemical reactions. Still, some reactions of carbonium ions mentioned in [3], like

$$CH_3CH_2CH_2^+ \rightarrow CH_3CH{=}CH_2 + H^+$$

could bring into the melt significant amounts of hydrogen ions that are both highly acidic and highly oxidizing.

The most commonly encountered impurities in chloroaluminate melts are products of hydrolysis. Anhydrous $AlCl_3$ as well as fused chloroaluminates react vigorously with water and traces of moisture are sufficient to produce contamination. A formal equation

$$AlCl_3 + H_2O = 2\ HCl + AlOCl,$$

shows the important features of such hydrolysis, even if it does not correspond exactly to the real process. Two kinds of products are formed: a hydrogen compound, which is HCl in equimolar MCl:$AlCl_3$ melts [46] and probably also in more acidic (higher pCl) melts, although this has yet to be proved. Next, a compound with an aluminum-oxygen bond is formed, possibly more complex than AlOCl. Tremillon and Letisse [46] assume that it is $Al_2OCl_5^-$, with a structure analogous to that of Al_2Cl_6. The high Al - O bond energy provides a thermodynamic driving force for the reaction.

Grothe and Piel [29] working in a chloroaluminate melt at 600°C observed a precipitation of aluminum oxide, which they believe resulted from the thermal decomposition of aluminum oxychloride. One may conclude from their findings that at lower temperatures the oxychloride would be fairly soluble, although possibly unstable thermodynamically. Tremillon and Letisse found that it is "neutral" in the acid-base sense (i.e., about as basic as $AlCl_4^-$ and distinctly more so than $Al_2Cl_7^-$). Oxygen-containing compounds are not eliminated by the various methods of melt purification (except possibly by electrolysis in some cases). They are not reported to have any direct adverse affect on electrochemical processes in the melt. Verdieck and Yntema [82] quote Marshall's thesis [48] stating that 1 mol% of dissolved oxygen-containing compounds does not alter the deposition potentials of metals in the ternary eutectic KCl - NaCl-

$AlCl_3$ melt.

Hydrogen compounds, in contrast to oxides and oxychlorides, do influence most chemical reactions in fused chloroaluminates. They are strong oxidizing agents. The standard electrode potential of the $H(I)/H_2$ couple has been determined in this thesis for a 64 mol% $AlCl_3$ melt at 135°C (see Table II). It has been known from the work of Yntema [82,83] to be higher than most of the standard potentials of M(I)/M(O) couples, including those of silver and mercury.

The high oxidizing power of hydrogen compounds made authors working in the field stress the importance of removing hydrolysis products from the melts. There is one notable exception: Howie and Macmillan [37] favor about 0.07 wt.% [0.2 mol%] HCl in the melt in order to obtain smoother cathodic aluminum deposits. Various purification procedures have been described, but no direct quantitative determination of hydrogen compounds has been attempted. Most authors seem to believe that they have eliminated hydrogen compounds "completely" and they support this with some indirect evidence. Corrosion studies, however, tend to contradict this, as will be explained in the next section.

Two general methods have been used to eliminate from chloroaluminate melts the products of their hydrolysis: reduction (by active metals or by electrolysis) and bubbling of an inert gas to eliminate HCl. Reduction by aluminum is

the most widely used and has been used in the work reported in this thesis; stronger reducing agents such as sodium would be consumed in displacing aluminum from the melt. When Howie and Macmillan [36] found it necessary at one stage to use sodium, the reasons might have been kinetic; for instance, as they had iron in the system, the aluminum surface could get blocked by an iron film [43]. In $AlCl_3$-rich melts at lower temperatures, the aluminum surface might also get blocked by solid aluminum chloride [35]. As a rule, however, the reduction by finely divided as well as by compact aluminum metal (usually wire) would work [2,82,84].

The use of nitrogen bubbling in $AlCl_3$-rich melts is, of course, very limited due to the volatility of $AlCl_3$; it cannot be carried out without causing uncontrolled changes in the melt composition by loss of $AlCl_3$.

Verdieck and Yntema [82,83] immersed an aluminum spiral in the melt for 4-6 hours and then electrolyzed with a graphite anode and a platinum cathode at a voltage less than 2 V until aluminum started to deposit on the cathode: this was interpreted as a sign of complete removal of hydrogen compounds.

Wade, Twellmeyer and Yntema [84] eliminated hydrogen compounds by electrolysis between platinum electrodes; with an impressed voltage of 1 V only hydrogen compounds were reduced (a current of 15-20 mA was recorded at an $8cm^2$ auxiliary cathode, indicating a current density of

2 - 2.5 mA/cm^2); when the current density dropped to 0.5 - 0.6 mA/cm^2, a marked rise of the potential was observed, and this was taken as an indication of a hydrogen-free melt.

Anders and Plambeck [2] used an aluminum spiral left in contact with the melt for one hour. Hames and Plambeck [32] purified a filtered KCl-NaCl-$AlCl_3$ eutectic by electrolyzing for several hours with platinum electrodes of 2 cm^2 in area and an imposed voltage of 2 V. They observed a current density decrease from 0.05 to 0.01 mA/cm^2 during this electrolysis.

Martin de Fremont and co-workers [50] in their studies with the dropping mercury electrode found that hydrogen compounds oxidize mercury; this effect disappears after the melt has been in contact with an aluminum spiral for 2-3 hours. Bubbling of nitrogen was not found satisfactory, because when an aluminum spiral was immersed into the melt after two hours of bubbling, gas bubbles, presumably hydrogen, could still be seen forming at the aluminum surface. The authors quote the thesis of M. Leroy, stating explicitly that hydrogen ions are formed within the melt from traces of humidity.

A purification procedure for the tetrachloroaluminate (50 mol% $AlCl_3$) melt is described by Trémillon and Letisse [46,81]. In spite of the higher temperature used (175°C) their system was considerably less volatile than $AlCl_3$-rich melts. This enables the authors to use bubbling of dry

inert gas in order to remove volatile hydrogen compounds. In their study of the $H(I)/H_2$ redox couple [46] they found a linear relationship between the potential of a hydrogen electrode and the pCl value of a given melt, which would be predicted by applying the Nernst equation to the reaction

$$HCl + e^- = 1/2\ H_2 + Cl^-,$$

while a simple reduction of hydrogen ions to H_2 would produce no dependence on the concentration of chloride ions. From this they concluded that no free hydrogen ions are present and that the only oxidized form of hydrogen in the melt is HCl. This is equivalent to saying that the solvent exerts a levelling effect and converts H^+ to HCl. Bubbling of dry nitrogen for 3 hours reduced the depolarizing current density for HCl on a 1 mm^2 rotating platinum microelectrode to 0.15 mA/cm^2. Bubbling combined with an addition of aluminum powder as a reducing agent caused a further decrease in current density to 0.02 mA/cm^2.

Groshev [27] found the solubility of HCl in $NaAlCl_4$ to be 8.5×10^{-6} mol/cm^3, i.e., 5×10^{-3} mol/kg or 0.1 mol%, at 160°C. This, according to his data, is 50-100 times higher than the solubility of chlorine or noble gases in this melt. The heat of dissolution is estimated as 6-17 kcal/mol. The reaction between aluminum and HCl is of first order with respect to HCl and its apparent activation energy is 11 kcal/mol Al. Unfortunately it is not quite clear from Groshev's description, whether solubility at an HCl partial

pressure of 1 atm. was in fact determined.

Howie and Macmillan [37] recommend making use of the reaction between hydrogen chloride and aluminum in the melt, which in their work was a near-eutectic $NaCl-AlCl_3$ melt, to obtain smoother cathodic deposits of aluminum and eliminate dendrites. They made no direct HCl determination and they estimate a concentration of 0.07 wt.% HCl (0.2 mol%) to be optimal.

Several authors did consider it difficult or impossible to eliminate products of hydrolysis from molten chloroaluminate system. They would, therefore, try to circumvent the "in-melt" purification step--either by an especially careful sublimation of aluminum chloride, as described for instance by Howie and Macmillan [36], or by an in-situ synthesis of aluminum chloride as described by Bjerrum, Boston and Smith [5]. This last approach has been adopted in some papers by Mamantov and co-workers [78]. It is worth noting that Bjerrum, Boston and Smith [5], as well as Groshev [27] favor the use of hydrogen chloride rather than chlorine in the aluminum cloride synthesis. Contamination by HCl is not regarded as a problem (as opposed to contamination by water!).

The difference in (standard electrode) potentials between hydrogen and aluminum being of the order of 1 V, one might expect a fast reduction of hydrogen ions, or dissolved HCl, by metallic aluminum; nevertheless, for reasons which

are not clear and may be connected with other melt contaminants (for instance organics), this does not occur, as far as traces of hydrogen compounds are concerned. When studying the properties of aluminum as a reducing agent in molten chlorides, Kogan and Rabovskii [43] found that freshly deposited metallic iron could block the aluminum surface preventing further reduction of iron compounds dissolved in the melt; such an effect, however, cannot be expected in the case of hydrogen. Also, when assessing the reducing power of metallic aluminum, it should be noted that in the presence of heavy metals the reduction by aluminum may be more complex: Kogan and Rabovskii [43] have, by X-ray diffraction, ascertained the presence of FeAl and Fe_3Al_5 in iron deposits on aluminum. Chovnyk and Polyantseva [12] report some evidence for the electrodeposition of CoAl and Co_2Al_5 from $KBr-AlBr_3$ melts.

Chloroaluminate melts are often studied at temperatures well above the eutectic melting point, but still below the melting points of the components. (Aluminum trichloride melts at about 190°C [39]; the KCl-NaCl eutectic at 661°C [51,63].) Under these conditions protracted electrolysis with an aluminum electrode can bring about a particular type of passivation phenomena, described by Holleck and Giner [35]: the composition of the melt in the vicinity of the electrode can be altered so much that the liquid range of the melt is exceeded, and solid deposits of either alkali

chloride or $AlCl_3$ then cover and block the electrode surface.

D. CORROSION IN MOLTEN CHLORIDES

Corrosion of metals in chloride melts, some of them containing aluminum trichloride, was studied by Russian workers [28,40,41,73] and found to depend largely on the presence of hydrogen-containing compounds, presumably mainly HCl. While most authors commenting on melt purity seem to believe that they have eliminated hydrogen compounds "completely" and support this by some indirect evidence, most corrosion studies [40,41] report a "substantial decrease" in metal corrosion rather than its complete elimination. Kochergin, Garpinenko and co-workers [41] working at 700°C in binary eutectic mixtures of chlorides of group 1 A and 2 A metals, were able to "almost eliminate" corrosion by adding magnesium or zinc metals and then restore the original corrosion behavior by saturating the melt with HCl gas. Kochergin and Stolyarova [42] speak about the "ability of fused salts to add HCl". Working in NaCl-KCl and LiCl-KCl systems they found that H^+ could not be removed by simply increasing the temperature; it was "almost completely" removed by metallic magnesium at 450°C under reduced pressure (10^{-5} mmHg).

Groshev, who has studied extensively the reaction between aluminum metal and hydrogen chloride in fused salts [25-27] dealt with the corrosion of iron in fused

chloroaluminates in his thesis [28]. Kogan and Rabovskii [43] quote him giving a rate of corrosion for iron in an unspecified NaCl-$AlCl_3$ melt at 200°C as 3.27 g/m^2h; this in presence of metallic aluminum decreases to 0.08 g/m^2h. Kogan and Rabovskii themselves [43] believe that the corrosion of iron causes a periodic loosening of iron films from an aluminum surface which occurs in melts containing $AlCl_3$. They also state that chloroaluminate melts are more corrosive than molten sodium chloride would be in comparable conditions.

Fink and Solanki [20] report strong corrosion of iron in fused chloroaluminates, but at the same time they consider nickel to be rather immune to corrosion. This may be explained by the fact that they used a nickel crucible as a cathode for the deposition of aluminum; it has been repeatedly observed here that iron, cobalt and nickel electrodes, on which more cathodic potentials had been impressed, revert only slowly, sometimes during several hours, to either their equilibrium or corrosion potentials.

Although corrosion in $AlCl_3$-containing melts has been reported and even measured [28,73], it should be kept in mind that spontaneous dissolution of metals like iron, cobalt and nickel in pure dry chloroaluminate melts is not favored thermodynamically. This can be seen from the values of standard electrode potentials [64]. Iron, the least "noble" of the three metals, has a standard potential

approximately +0.6 V against the aluminum electrode (see Table II). All corrosion must therefore be related to the presence of some oxidizing species in the melt; even the residual corrosion in the presence of aluminum metal should be viewed as resulting from incomplete purification.

Corrosion by hydrogen compounds, on the other hand, is perfectly predictable from standard potential data, as pointed out by Martin de Fremont et al. [50]. These authors actually proved that metallic mercury was oxidized to the monovalent state by products of melt hydrolysis. The assumption that corrosion is caused by HCl is compatible with most of the published work, including reports about partial suppressing of corrosion by methods used to purify the melt [28,46,50]. The use of nitrogen bubbling, even if its success was only partial [46,50], points to the fact that volatile hydrogen-containing impurities, mainly HCl, are the ones to be eliminated. Studies of mixed chloride-fluoride melts by Kochergin and Davydova [40] showed, however, some corrosion of iron due to non-volatile compounds, probably hydroxides, that could not be removed by vacuum treatment.

E. MONOVALENT ALUMINUM COMPOUNDS IN THE MELT

Recent work by Delimarskii et al. [16] and Storozhenko [74] has dealt with the presence of monovalent aluminum compounds in chloroaluminate melts. While compounds of Al (I) are usually not stable at lower temperatures and

undergo disproportionation, it would not be surprising to see them stabilized to some extent in "acidic" chloroaluminate melts, which are known to stabilize lower valences of metals generally. Referring to the earlier discussion of the Lewis-acid character of aluminum trichloride and the scarcity of chloride ions (electron donors or Lewis bases) in $AlCl_3$-rich chloroaluminate melts, there is no reason to believe that the stabilizing effect of these melts on low-valence compounds would be limited to transition metals. In fact the results of Anders and Plambeck [2] concerning the stability of monovalent gallium compounds in the KCl-NaCl-$AlCl_3$ eutectic would quite logically point towards the existence of non-negligible equilibrium amounts of monovalent aluminum compounds in the same melt. Some chemical evidence for the presence of a reducing aluminum compound in the melt has been found by Anders [1] and by Midorikawa [55] and Notoya [60], who observed metal transport and recrystallization of aluminum in NaCl-$AlCl_3$ melts.

It seems more difficult to accept the quantitative conclusions of Storozhenko [74], who gives the fraction of aluminum present in the monovalent state at equilibrium as approximately 5 mol%. His results are based on determinations of chemical solubility of aluminum metal in various NaCl-$AlCl_3$ melts; such determinations would be radically affected by the presence of traces of oxidizing impurities or by the existence of chemical transport caused by a local

temperature gradient. Thonstad [75] investigated the solubility of aluminum in Al_2Br_6 and Al_2I_6 and came to the conclusion that Al(O) existed in solution rather than Al(I). It is probably wise to consider Storozhenko's values only as upper limits of aluminum solubility or of the mole fraction of monovalent aluminum in the melts concerned.

Literature data are scarce concerning the interaction of hydrogen compounds and Al(I) compounds in chloroaluminate melts. Delimarskii and co-workers [16] observed the formation of gas bubbles on an aluminum anode, when the chloride-based electrolyte contained some moisture. Belyaev and Firsanova [4] state that monovalent aluminum reacts with water,

$$2\ H_2O + Al^+ = Al^{3+} + H_2 + 2\ OH^-.$$

In general, it is to be expected that the presence of hydrogen compounds would lower the concentration of monovalent aluminum. It would therefore also prevent chemical precipitation of aluminum metal by disproportionation of Al(I) compounds and this could account for the smoother electrochemical aluminum deposits found by Howie and Macmillan [37] in the presence of hydrogen ions.

F. ELECTRODE POTENTIALS

In 1940 Plotnikov, Kirichenko and Fortunatov [65] established an electrochemical series of metals in an equimolar sodium chloride-aluminum chloride bath at 400-600°C.

This was followed by a series of quantitative studies by Yntema and his students [49,82-84,86] involving more than twenty metals. Most of their data were later confirmed by Martin de Fremont et al. [50] and by Plambeck and co-workers [1,2,31,32].

Yntema's method consisted in determining the potentials of electrodes during the process of metal deposition on their surface. These potentials were measured at various current densities in a three-electrode arrangement which prevented polarization of the reference electrode and were extrapolated to zero current. Yntema and co-workers were using 1 mol% solutions of metal ions in the KCl-NaCl-$AlCl_3$ eutectic melt and their data were taken by subsequent authors [50,64] as estimates of equilibrium electrode potentials at that concentration and temperature, temperature being 156°C in most of Yntema's measurements. Yntema was using platinum electrodes, but these certainly became covered by a surface layer of the deposited metal during the initial stage of each run. His current-potential curves intersect the potential axes (i = 0) at values equal to the equilibrium potentials of the reaction

$$M^{n+} + n\ e^- = M(\text{standard state of pure element}).$$

Approximate values of standard potentials can then be calculated from these estimated equilibrium values using the Nernst equation, as was done by Plambeck [64].

Martin de Fremont and co-workers [50], also working

in the ternary eutectic melt, used polarography with a dropping mercury electrode and determined half-wave potentials for the reduction of metal ions. Hames and Plambeck [32] were the first to attempt direct potential measurements, using metal electrodes in equilibrium with melts containing known amounts of metal ions. Their values were in very good agreement with those of Yntema in the cases of zinc, mercury and silver. The case of cadmium proved to be more complex, due to an equilibrium between Cd^{2+} and Cd_2^{2+} in the melt. The standard potential values for $Cd^{2+}/Cd°$ reported in [32], as well as those from direct potential measurements in [31] are significantly lower than those of Yntema.

Anders and Plambeck [2], in extending the direct potential measurements to metals of groups I b and III b, usually either confirmed Yntema's values or could well explain the discrepancies, such as the case of gallium, where stable univalent gallium was not known to exist in 1940 [1]. Some irregularities pointing to the formation of polyatomic ions were observed in the case of silver. Such polyatomic ions are well known, for instance bismuth forms them in chloroaluminate melts [5-7,14,78] and so does mercury [76].

In this thesis an attempt was made to apply the direct potential measurement method to the first triad of group VIII transition metals: iron, cobalt and nickel.

Quantitative data about the electrochemical behavior of these metals in chloroaluminate melts are rather scarce. The only published material on electrode potentials comes from the teams of Yntema [82,83] and Martin de Fremont [50]. Both groups of authors agree as far as nickel is concerned. The polarographic wave of nickel is well developed [50] and has some characteristics of a fast electrochemical system. On the other hand, the polarographic reduction of iron and cobalt occurred at potentials that were some 0.2 V more negative (cathodic) than expected from [82] and the waves were much more poorly defined than in the case of nickel. While both sets of data have essentially been obtained from measurements of reduction processes of iron and cobalt ions, those of Yntema [82] should be preferred for two reasons:

1. The metal deposition in [82] took place mostly on surfaces already covered with the metal studied; it is more credible to take the activity of such a layer as equal to one than it is in the case of [50], where a mercury drop was involved; the solubilities of iron and cobalt in mercury are very small, less than 10^{-5}% [33]. Under these conditions, the activities of iron and cobalt become somewhat uncertain. In the case of nickel, there exists a compound $NiHg_4$, stable below 300°C [33].

2. Yntema's set of potential values for iron, cobalt and nickel fits better with values in other chloride melts, where cobalt and nickel always exhibit a rather similar behavior

(see data in [64]).

Although the experiments of Verdieck and Yntema [82] were not repeated here, estimates of deposition potentials were made from voltammetric data (Table VII); these fit well with the results in [82]. Possible implications of this will be discussed later.

Verdieck and Yntema [82,83] determined the deposition potential of hydrogen in the KCl-NaCl-$AlCl_3$ eutectic at 150°C. Their melt had a formal concentration of 1 mol% H^+. Some compensation of errors might have occurred: hydrogen ions were added as $AlCl_3.6\ H_2O$ and considerable evolution of HCl gas was observed, but the amount of hydrated salt used, 1.34 g or 0.07 H equivalents in 73 g or 0.7 moles of melt, was nearly one order of magnitude above the theoretically required quantity. A value of 1.05 V was proposed for the deposition potential of hydrogen, implying fairly strong oxidizing properties of the hydrogen ion.

Wade, Twellmeyer and Yntema [84] give a value closer to 1.15 V. In their experiments no water was added, but anhydrous hydrogen chloride was passed over the melt, which was stirred to allow dissolution of the gas. Their data seem less reliable because they used a platinum reference electrode, which is sensitive to changes in the concentration of hydrogen compounds. Wehrmann and Yntema [86] report a deposition potential of 1.05 V for hydrogen in the analogous bromide melt (66 mol% $AlBr_3$, 20 mol% NaBr, 14 mol% KBr).

Martin de Fremont et al. [50] confirm the oxidizing properties of hydrogen ions in this melt as reported by Verdieck and Yntema [82]. They observed the oxidation of the mercury dropping electrode in melts which contained traces of humidity. Mercury was also oxidized in their experiments by Fe^{3+}; this is in agreement with the polarographic reduction of Fe^{3+} to Fe^{2+} reported by Chovnyk and Myshalov [11].

The results of Trémillon and Letisse [46,81] have to be applied with some caution, as they were obtained in an equimolar NaCl:$AlCl_3$ melt and not in an "acidic" one. Their reference electrode was aluminum in a saturated solution of NaCl in $NaAlCl_4$. The potential of this electrode can, however, be related to the usual reference potential(s) of aluminum in eutectic or near-eutectic melts through the study of concentration cell voltages, done by Fannin, King and Seegmiller [18,19].

Trémillon and Letisse found that hydrogen gas is soluble enough in the melt, that current-potential curves of the hydrogen system can be recorded. They also found a bare platinum electrode functioning satisfactorily as a hydrogen electrode. In their experimental work [46,81] hydrogen was produced directly in the melt by reducing hydrogen compounds with aluminum powder. When anhydrous barium hydroxide was added, its hydrogen was reduced by aluminum and the "base"

equivalent of the oxide ions introduced could be coulometrically titrated.

CHAPTER II

EXPERIMENTAL

1. Reagents

Aluminum chloride, (certified reagent grade, Fisher Scientific Co., Ltd.) was purified as described by Anders [17] in order to eliminate iron compounds and the bulk of hydrolysis products, as follows: About 250 g of aluminum chloride, covered by a 1 cm thick layer of granular aluminum metal (reagent grade, 30 mesh, Fisher Scientific Co.), were heated in a 40 cm long Pyrex ampoule, 5 cm in diameter, isolated from the surrounding atmosphere by a mercury pressure relief valve. The upper part of the ampoule was cooled by a stream of compressed air. The aluminum chloride condensed as a colorless or snow-white polycrystalline solid in the part of the ampoule just above the granular aluminum layer. A slowing of the sublimation process was usually observed after about three hours as the diffusion of gaseous aluminum chloride was progressively blocked by the mass of crystals growing from the cooler ampoule walls towards the center. After four hours the sublimation was interrupted with usually about one quarter of the original batch remaining at the bottom of the ampoule.

No attempt was made to increase the yield of this sublimation process by raising the temperature, because this might increase the volatility of iron chlorides and oxygen-containing compounds and bring some of them into the pure product. The ampoule was placed inside a glove box filled with dry nitrogen, and broken. All of the sublimed aluminum chloride was used immediately for melt preparation, except a surface layer contaminated with baked-in aluminum metal; this was separated mechanically with a knife and discarded.

Sodium chloride (AnalaR, BDH Chemicals, England) and potassium chloride (reagent grade, McArthur Chemical Co., Montreal) were dried at 100°C under vacuum for several hours, whenever necessary. In some of the experiments, however, this was omitted, because the aluminum chloride used was not completely free of its hydrolysis products and was by far the greater source of hydrolytic impurities in the melt. These can, of course, be readily detected by voltammetry [78].

The electrode metals were obtained in wire form, about 1 mm in diameter, of 99.99% purity, from A. D. MacKay, New York. Aluminum wire, 1.6 mm in diameter, was obtained from E. H. Sargent and Co. For larger auxiliary electrodes at which no measurements were made, iron, nickel, zinc and aluminum sheet metals of commercial purity were used after

cleaning, degreasing and drying.

Barium chloride dihydrate (assay over 99%, May and Baker Ltd., Dagenham, England), was used without further purification as a source of known amounts of water. Anhydrous barium hydroxide was prepared from BDH AnalaR $Ba(OH)_2 \cdot 8 H_2O$ (assay 98%) by pumping away the water at room temperature for 20 hours and then heating the batch at 100°C for 24 hours under continued pumping. This procedure has been used and recommended by Seward [70]. The purity of the product was checked by a titration with standard HCl and was found to be 98.8%.

Ferric oxide was prepared from ferrous ammonium sulfate $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ (which was the purest iron compound readily available) by oxidation with nitric acid, precipitation by ammonium hydroxide and washing with concentrated ammonium chloride followed by distilled water.

2. Melt Preparation

The compact sublimed aluminum chloride was ground inside the glove box and transferred into a tightly stoppered conical flask; this was then removed from the glove box, weighed and quickly returned to the box. The calculated amounts of sodium chloride and potassium chloride were then added to make up the desired melt composition. Virtually all the experiments were run in a melt whose composition was 64 mol% $AlCl_3$, 22 mol% NaCl and 14 mol% KCl. A few

preliminary measurements were done in a melt composed of 66 mol% $AlCl_3$, 20 mol% NaCl and 14 mol% KCl, which had been used in previous work in this laboratory [1,2,31,32].

The mixture of chlorides was melted in a round bottomed flask using an electric heater and transferred into the thermostated electrochemical cell inside the glove box. A yellow or light brown coloration of the melt was usually noticed, in agreement with previous work [1,50,81], although once or twice the resulting liquid was colorless, with a small amount of black precipitate which could be filtered off. The cause of the coloration is not known; it may be due to carbon from organic material [56] or dissolved silicon compounds [21]. Hydrogen chloride or chlorine were found to produce additional melt darkening [1]. According to Boston [8] in the case of hydrogen chloride this might be due to acetylenic impurities present in the gas. Some authors suggest [46] that clearing up of the liquid phase and adsorption of the colored material occurs on contact with metallic aluminum. This was also observed in the present work, but the clearing up took several hours and was not complete. The color shade and intensity were unrelated to the results of electrochemical measurements in these melts.

Voltammetric tests, in agreement with previously published data [31,46,50,78], showed that further purification of melts prepared in this way was necessary, mainly

with regard to the presence of electroactive compounds, which presumably arise from the reaction of aluminum chloride with moisture. This is discussed in detail later in this thesis. Immersion of an aluminum spiral into the melt for three hours as used by Anders [1], did not eliminate these hydrogen compounds completely. Their concentration did, however, decrease by about one order of magnitude to a steady-state value, which could not be further lowered by contact with metallic aluminum. In view of this result, a three hour reduction of the melt by an aluminum spiral inside the cell, as well as voltammetric checks on the presence of hydrogen compounds as suggested in [78], were made a part of the standard melt preparation procedure which preceded all measurements.

It is possible to filter the melt [31,32],before bringing it into the cell. In most of the experiments reported in this thesis, however, filtration was unnecessary, because the working as well as the reference electrodes were located in separate compartments which the melt entered through sealed frits; it was thus filtered automatically.

3. Cell

This was contained within the glove box and is identical to that described in detail by Hames [31]. An oil jacket contained circulating paraffin oil from a NB-ELE thermostat (Colora, West Germany). Temperature was kept

at 135 ± 1°C unless otherwise specified. Half-cell compartments were glass tubes 1.3 or 2.5 cm in diameter with fritted bottoms (10 - 20 μ porosity; Ace Glass Inc., Vineland, N.J.).

4. Apparatus

Potentials were measured with a 3440A Hewlett-Packard digital voltmeter. Coulometric oxidations and reductions were performed with a Model IV Coulometric Current Source (E. H. Sargent and Co.). Polarizing voltages on the working electrode were monitored and coulometric currents adjusted in order to remain within the potential limits of the melt.

A modified Sargent Model FS polarograph with a Model XV motor was used for voltammetric measurements.

A Wenking 66 TS-1 potentiostat (G. Bank, West Germany) served to obtain stationary current-voltage characteristics in a three-electrode arrangement.

A Bausch and Lomb Spectronic 20 single-cell visible-range spectrophotometer was used in the determination of iron.

5. Electrodes

Aluminum wire was used as a reference electrode. The suitability of such an electrode was discussed and demonstrated by several authors [32,65,82] and it is now generally accepted as the standard reference electrode in

chloroaluminate melts [9]. Schulze and Hoff [69] give the exchange current density of this electrode as 20.6 A/cm^2; this means that the electrode is essentially unpolarizable. The potential of this electrode in a pure chloroaluminate melt is defined as zero. This potential actually depends on the mole fraction of aluminum chloride in the melt; from the discussion of this problem by Boxall, Jones and Osteryoung [9] it can be inferred that a 1 mol% change in the formal aluminum trichloride content would correspond to a potential difference of 3 - 7 mV in near-eutectic (NaCl: 2 $AlCl_3$) melts.

Electrodes for stationary potential measurements (iron, cobalt, nickel, zinc, and platinum for hydrogen potential measurements), which were also used for coulometric generations of divalent metal ions, were prepared by winding 0.8 mm metal wires into small spirals. The immersed geometric area of these electrodes was 2 - 3 cm^2.

For voltammetric measurements a 0.003 cm^2 platinum microelectrode was prepared by sealing a piece of 0.6 mm platinum wire into a Pyrex glass tube followed by cutting and grinding both metal and glass to a flat area. This electrode was repolished with fine emery cloth whenever necessary.

Electrodes used for internal or as auxiliary electrodes were typically aluminum, iron or nickel plates, 3 x 4 cm,

0.8 - 1 mm thick.

All electrodes were degreased by chloroform or carbon tetrachloride, washed with dilute hydrochloric acid and water, and dried before use.

6. Analytical Methods

Direct voltammetry with a stationary platinum microelectrode has the advantage of being applicable virtually at any time during a series of measurements. It was not generally relied upon as a method of quantitative determination of iron, cobalt and nickel in the melt, due to the low precision of voltammetric reductions to insoluble materials on solid electrodes. It was, however, used successfully to detect the presence of small amounts of these metals in the molten systems. Trial voltammograms with coulometric generation of the respective metal ions showed a limit of detection around 10^{-4} on the mole fraction scale (0.01 mol%). Because an anodic stripping procedure could easily be used at least semi-quantitatively in this system, the limit of detectability for iron, cobalt and nickel was in fact a mole fraction of 10^{-5} (0.001 mol%).

In order to get comparable results, these voltammetric runs were performed in a uniform way: cathodic polarizing sweeps (dE/dt = 100 mV/min.) were carried up to a potential 200 - 250 mV below the cathodic peak value; there, the electrode potential was kept constant for 30 seconds and

then anodic stripping started with the same speed.

The voltammetry of hydrogen compounds is discussed in detail elsewhere in this thesis.

Whenever standard additions of chemicals between measurements were necessary, known amounts of solid reagents (usually of the order of 100 mg) were placed in small glass vials, which fit into a hole in the Teflon cell stopper. During such a reagent addition the cell would be opened to the dry-box atmosphere for about 1 second, as a glass plug was taken out and the reagent-containing vial brought in. Water was added in the form of $BaCl_2 \cdot 2 H_2O$ crystals.

For further analysis outside the glove box, the whole content of one compartment or a sample of the bulk melt was transferred into a clean dry beaker, allowed to cool and solidify, taken out of the dry box and weighed immediately. It was then dissolved in water; sometimes an addition of dilute acid proved necessary to speed up dissolution.

The standard α, α' - dipyridyl method was used for the spectrophotometric determination of iron [72]. Only total iron was determined, i.e. reduction by hydroxylammonium chloride preceded the addition of the color-forming reagent. Large amounts of aluminum compounds are known not to interfere with this determination [57,72].

CHAPTER III

RESULTS AND DISCUSSION

A. STANDARD STATES, UNITS AND CONVENTIONS USED

When values of standard electrode potentials are reported, some conventions regarding standard states are necessary. In agreement with the conventions generally used [61] the standard states referred to in this thesis are:

1. all pure elements and compounds in the form (modification), which is the most stable at the given temperature;

2. gases at a pressure of 1 atmosphere (neglecting the difference between pressure and fugacity);

3. species in solution in a hypothetical state, which combines unit concentration on the concentration scale used (mole fractions, if not stated otherwise) with properties of the species at infinite dilution in the molten solvent.

It is useful [1] to make an exception to rule 3 and state:

4. species that are constituents of the solvent melt or are linked to such constituents by a non-electrochemical equilibrium (e.g. Al^{3+}) are considered to be in

their standard state in whatever actual state they occur in the pure melt.

These definitions are compatible with conventions used in other melts [64].

If standard states are defined in this way, the actual potentials of aluminum electrodes in chloroaluminate melts automatically become standard potentials; this in turn is equivalent to defining the zero of the potential scale as the potential of a physical aluminum electrode in the pure melt. It is interesting to note that the melt exerts a "redox levelling effect" on the electrode potentials of metals that would hypothetically be stronger reducing agents than aluminum. In contact with the melt these metals get covered by a surface layer of metallic aluminum and therefore acquire a zero potential against the aluminum reference electrode. Thus negative equilibrium electrode potentials are not realizable. All actual equilibrium potentials are positive in sign and therefore all increases (or decreases) in potential values imply increases (or, respectively, decreases) in the potential difference against the aluminum reference electrode. A potential that is increasing is getting more anodic, more positive and more distant from the value for aluminum on the scale of potentials.

Each chloroaluminate melt, of course, implies a different Al(III) / Al(0) potential and therefore also a different scale of potentials according to these accepted rules. Some empirical correlation among these scales is available from recent studies of the voltages of concentration cells [9,18,19,77].

Fannin et al. [18] as well as Boxall, Jones and Osteryoung [9] approached the establishing of a true thermodynamic link among various chloroaluminate melts by studying chemical equilibria between selected aluminum-containing species in these melts. They had to use some approximations, such as neglecting junction potentials and assuming that Na^+ is the only current carrying species in NaCl - $AlCl_3$ melts, but that does not impair the practical validity of their results. In ternary melts as the one used in this thesis, Na^+ is partially replaced by K^+; the aluminum-containing species, however, remain the same [67] and similar electrochemical properties may therefore be expected.

The use of empirical relationships between data in different molten systems has been considered justified as long as this is the only way that makes possible some comparisons of results obtained in various melts. In this thesis, however, such comparisons were never involved in the actual presentation of experimental results.

All reported numerical data resulted from measurements actually performed in the near-eutectic ternary melt composed

of 64 mol% $AlCl_3$, 22 mol% NaCl and 14 mol% KCl, at the temperature of 135°C. When, as in the preliminary stage of this work, slightly different experimental conditions were chosen, the results are reported with an appropriate explanatory comment. In other words, no mathematical transformation of data which would compensate for differences in temperature or melt composition has been attempted.

References to various other chloroaluminate melts and other temperatures cannot be avoided, if comparison with the results of other authors' measurements is sought. Here the question arises, what magnitude of change in electrode potentials should be expected to result from small changes in either temperature or melt composition. Anders [1] has measured several electrode potentials as functions of temperature and he usually found a negative slope (more cathodic potentials at higher temperatures) of the order of 0.5 mV/°C. From the work of Boxall, Jones and Osteryoung [9], although it was done at 175°C in a binary NaCl - $AlCl_3$ system, we may accept the conclusion that the potential of an aluminum electrode should increase (get more anodic) by 3 - 7 mV, when the amount of $AlCl_3$ brought into the melt increases by 1 mol% (in the "eutectic" region, from 64 to 65 mol% $AlCl_3$). Given the role of temperature as a variable in the Nernst equation, the shift might be slightly smaller at 135°C. In our work, we did find small differences, of

the order of 5 mV, between potentials of metal electrodes in 64 mol% and 66 mol% $AlCl_3$ melts. This result however, should not be over-emphasized, because the melt composition may have been affected by a partial evaporation of aluminum chloride and because both the metal electrode and the aluminum reference electrode may respond to changes in melt composition.

In the reporting of results, a proper choice of the concentration scale is of some importance. Molarity, molality and mole fractions have all been used in molten salt work. In actual experiments with molten salts, concentrations are mostly set on the weight per weight basis; the density of the melt must be known, if the molarity scale is to be used and the mean molecular weight of the melt must be calculated, if concentration is to be given in mole fractions or mole per cent. In the case of chloroaluminate melts, where the density is often known to only two significant figures, the use of the molarity scale might imply a slight loss of precision. The other two scales are both perfectly suitable for work in chloroaluminate melts; the mole fraction scale was chosen in this thesis, because comparisons of the properties of different melts seem more meaningful when worked out entirely on mole basis and because solution equilibrium constants are conveniently obtained as plain numbers when this scale is used.

In general, it will be assumed in this thesis that all activity coefficients are constant; this is certainly justified as far as metal and hydrogen ions are concerned in view of their low concentration (less than 1 mol%) in all actual measurements. The calculated standard potentials refer to an extrapolated unreal state anyway and for the purpose of calculation it is more convenient to base them on unit concentration than on unit activity. Boxall, Jones and Osteryoung [9] used a variable activity coefficient for the $AlCl_4^-$ ions, but at the same time rejected using one for the $Al_2Cl_7^-$ species, which is present at about the same concentration level. In view of the definition of standard states given above, the question of using activity coefficients of these anions for the calculation of standard potentials does not arise in this thesis.

According to the IUPAC "Stockholm" sign convention, all potentials in this thesis are expressed as numerically equal to the electromotive force of the electrode half-reaction, written as a reduction process [44]. The tolerances shown are standard deviations.

B. METAL - METAL ION ELECTRODES

1. Measurements of Equilibrium Potentials

Direct measurements of the potentials of metal electrodes against the aluminum reference electrode were

always made by taking a series of four or more points in one and the same batch of melt. Between two successive measurements, the concentration of the metal ion in the compartment surrounding the metal electrode was increased by coulometric oxidation of the metal. Before each measurement enough time was allowed for the system to reach equilibrium (usually 15 - 25 min.). Potential readings stable for 10 minutes to ± 1 mV were taken as an indication that equilibrium has been established. A value of the standard potential was calculated from each measurement separately, using the Nernst equation. The actual equilibrium potentials were plotted against the logarithm of the amount of metal ions generated (Fig. 1, 2, 3). Such graphs have the same form as plots of potentials against the logarithm of concentration (classical Nernst plots), because logarithms of the two independent variables, amount of ions and concentration, differ only by an additive constant, as long as the amount of melt in the compartment does not change. In our experimental set-up this amount of melt was determined after the completion of each series of measurements; up to that time it represented an unknown constant and thus prevented the use of classical Nernst plots as working graphs.

As can be seen from Figures 1, 2 and 3, the plots were linear with the exception of points obtained at concentrations below approximately $X = 10^{-3}$ (the compartments

Figure 1

Equilibrium Potentials of the Iron Electrode

Points indicate observed values of equilibrium potentials in two separate experiments; the two lines are drawn with the theoretical slope for n = 2, which is 40.6 mV per log unit.

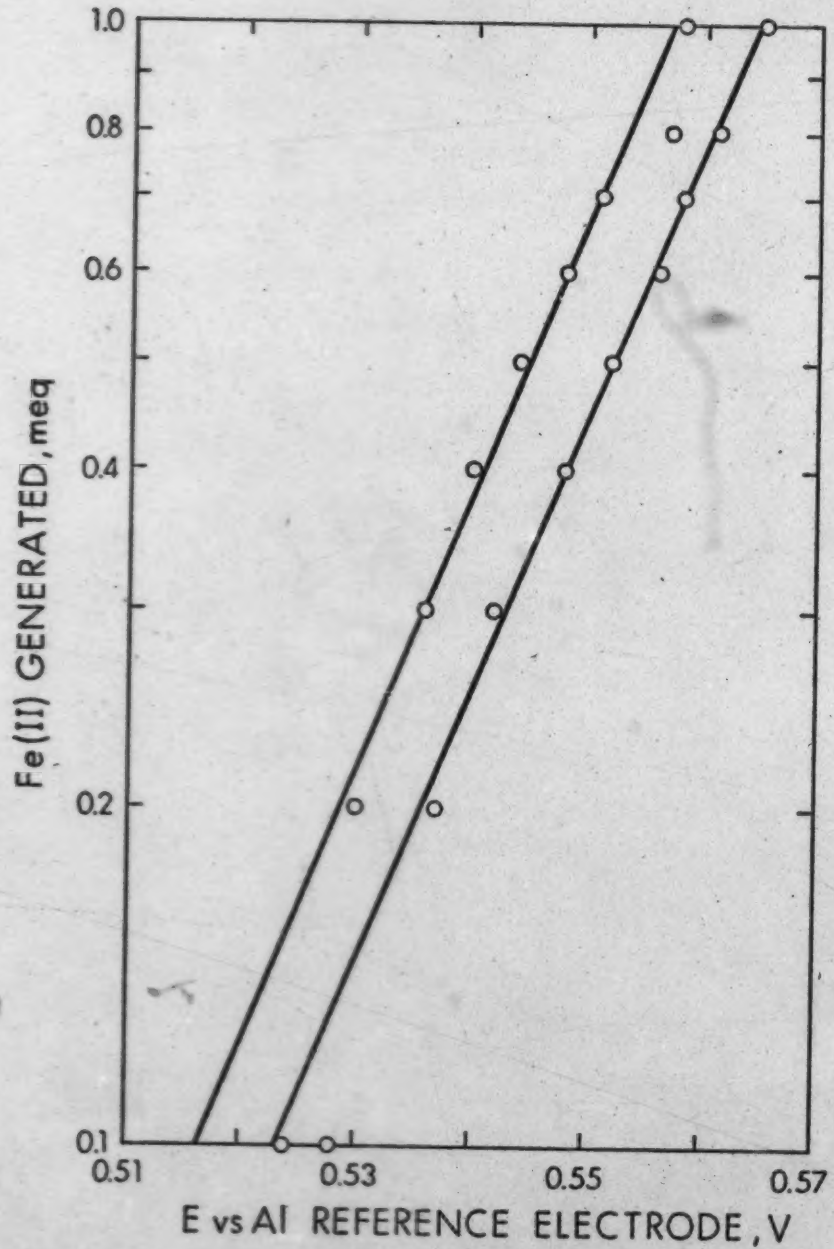

1.0
0.8
0.6
0.4
0.2
0.1
Fe(II) GENERATED, meq
0.51
0.53
0.55
0.57
E vs Al REFERENCE ELECTRODE, V

Figure 2

Equilibrium Potentials of the Cobalt Electrode

Points indicate observed values of equilibrium potentials. The line is drawn with the theoretical slope for n = 2, which is 40.6 mV per log unit.

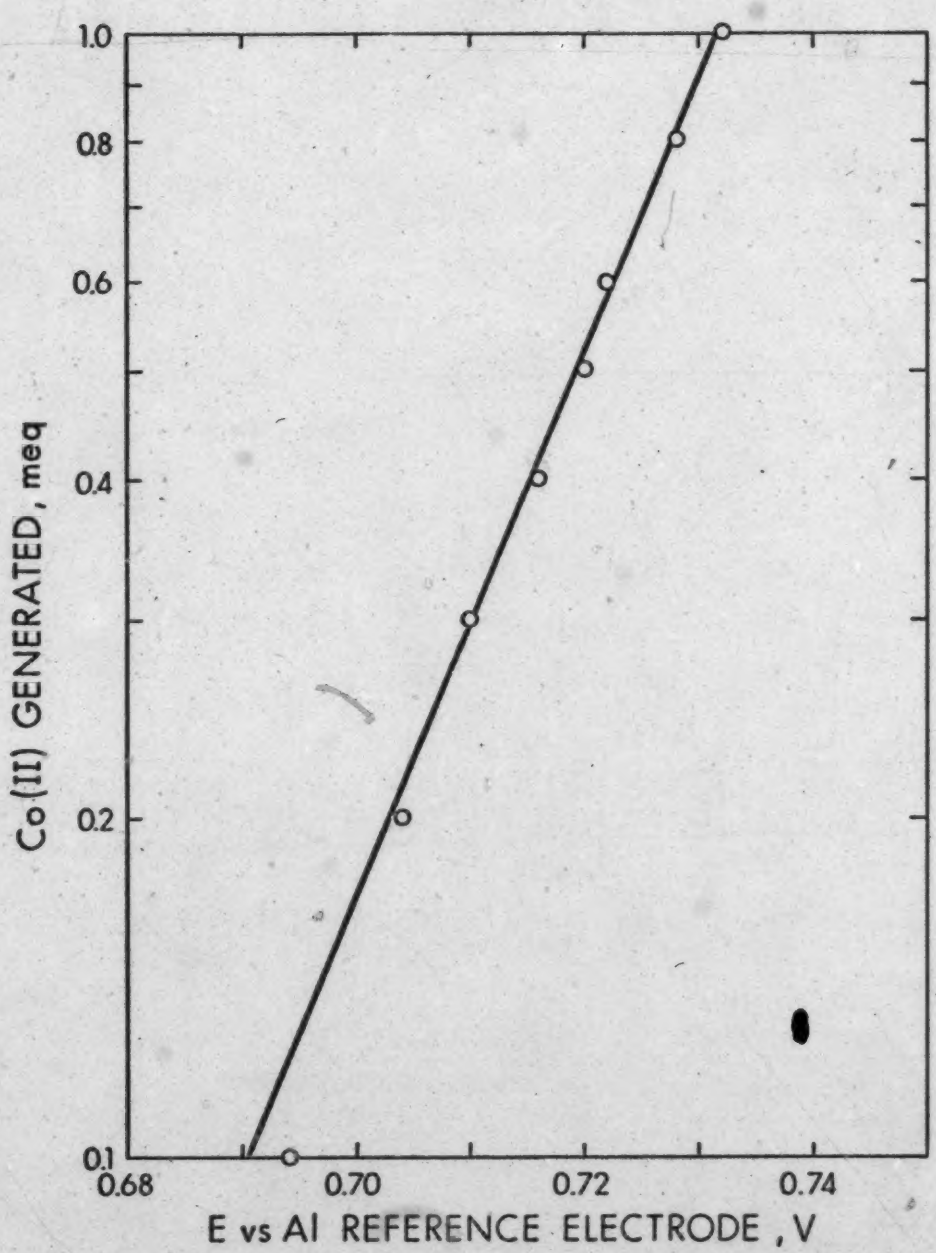
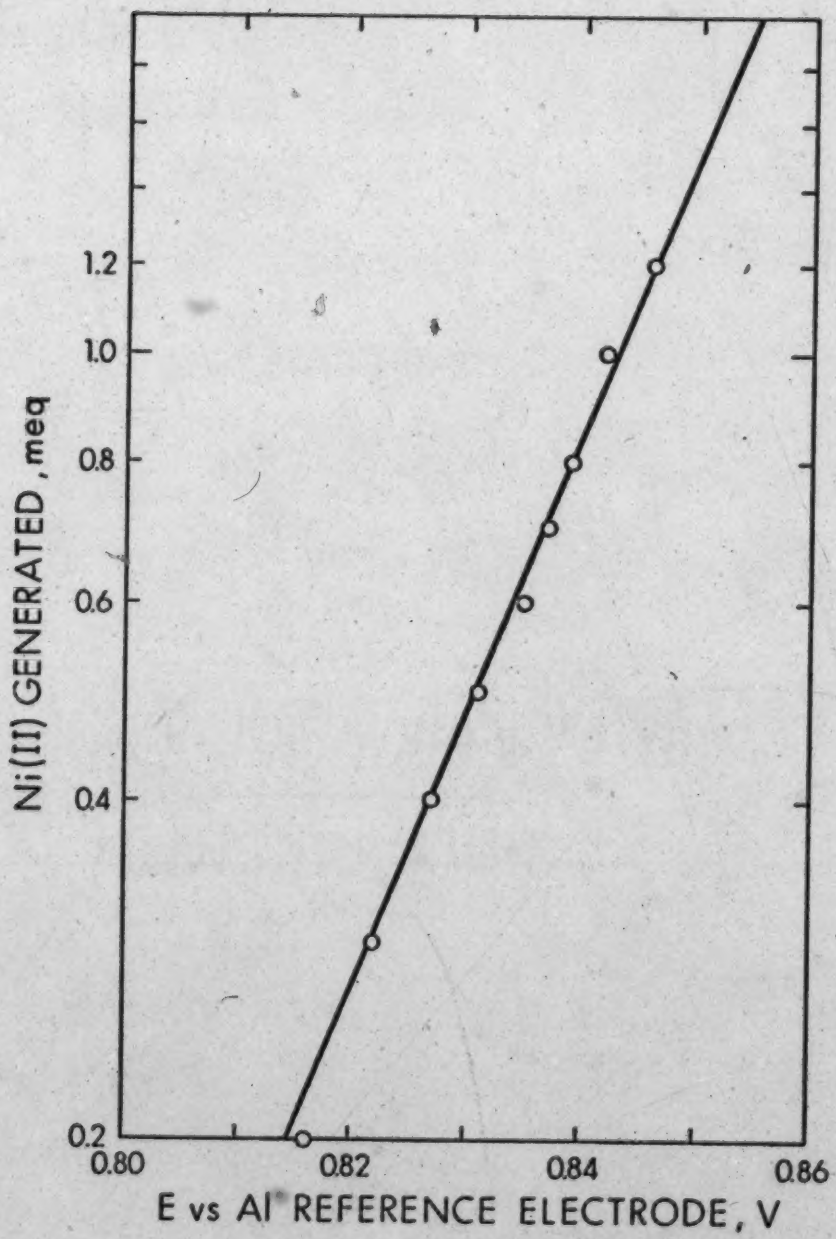

1.0
0.8
0.6
0.4
0.2
0.1
Co(II) GENERATED, meq
0.68
0.70
0.72
0.74
E vs Al REFERENCE ELECTRODE , V

Figure 3

Equilibrium Potentials of the Nickel Electrode

Points indicate observed values of equilibrium potentials. The line is drawn with the theoretical slope for n = 2, which is 40.6 mV per log unit.


Ni(II) GENERATED, meq
1.2
1.0
0.8
0.6
0.4
0.2
0.80
0.82
0.84
0.86
E vs Al REFERENCE ELECTRODE, V

usually contained about 0.1 mole of melt). Only points that fell within the linear part of the E vs. log N graph (N is the number of moles of metal ion generated) were used in calculating a mean value of the standard potential in each series of measurements. Standard potential values reported in this thesis (Tables II and III) are average results of two or more such series.

From the slopes of the linear segments of Nernst plots one can calculate the number of electrons, n, involved in the electrochemical oxidation. The following values of n were found by experiment:

Couple		n
Fe(II) / Fe(O)		2.0 ± 0.2
Co(II) / Co(O)		2.1 ± 0.1
Ni(II) / Ni(O)		2.1 ± 0.1
Zn(II) / Zn(O)	(one Nernst plot only)	2.0

When it became apparent that ferrous metals are corroded in contact with the melt as explained in Section B3 of this chapter, it was decided to find the true concentration of iron (II) compounds in the electrode compartment by an independent method and in this way include in the measurements any iron compound that may be present in the melt as a result of corrosion. Iron in the molten salt phase was then determined spectrophotometrically after

the termination of in-melt measurements. The reported standard potential value in this case is an average of eight single-point measurements.

Standard potentials for the iron, cobalt and nickel couples, as found in this thesis, are shown in Table II. The table also includes results for the $H(I)/H_2$ couple that is discussed later in the text.

Table III provides a comparison of these and other direct-measurement results with standard potential values determined from deposition potentials, as measured by Yntema and his students [82-84]. A general trend is visible from this table: direct potential measurements usually yield values of standard potentials slightly (up to 0.05) lower than those predicted from deposition potentials. A reversal of this trend is observed in the cases of mercury, iron, cobalt and nickel. At the same time, voltammetric and spectrophotometric analyses of the melt showed that iron, cobalt and nickel are corroded during the experiments. This was further investigated and it will be discussed later in this thesis in more detail. It should be stressed, however, that a simple increase in the concentration of transition metal ions, due to corrosion, can in no way account for the reported high values of standard potentials. This can be seen from the Nernst equation: at 135°C, the doubling of the concentration of a divalent metal ion would cause an increase

Table II

Standard Electrode Potentials in the KCl-NaCl-$AlCl_3$ Melt as Determined in this Thesis

Electrochemical Couple	E°(volts)	Standard Deviation	Note
$H(I)/H_2$	1.202	0.005	
$H(I)/H_2$	1.226	0.006	a
Fe(II)/Fe(O)	0.652	0.003	
Fe(II)/Fe(O)	0.645	0.005	b, d
Co(II)/Co(O)	0.841	0.003	c
Co(II)/Co(O)	0.827	0.002	b, c
Ni(II)/Ni(O)	0.927	0.002	
Ni(II)/Ni(O)	0.928	0.005	b
Ni(II)/Ni(O)	0.927	0.003	e

a. melt not properly saturated with hydrogen gas; see section C 2 of text

b. melt consisted of 66 mol% $AlCl_3$, 20 mol% NaCl and 14 mol% KCl

c. two different batches of cobalt wire were used; control experiments indicate that the difference in E° may be due to variations in wire quality rather than differences in melt composition. The value E° = 0.827 is probably to be preferred: the potential drift was smaller and the result is closer to the value of 0.820, obtained in one experiment with a cobalt-plated electrode.

d. from five runs, each with four or more points: concentrations calculated from generated amounts of Fe(II) without a spectrophotometric check

e. overall average of values obtained for this couple; there was no significant difference in the potentials measured in a 64 or 66 mol% $AlCl_3$ melt.

Table III

Standard Electrode Potentials in $AlCl_3$-NaCl-KCl Melts
[a] 64 mol% $AlCl_3$, 22 mol% NaCl and 14 mol% KCl
[b] 66 mol% $AlCl_3$, 20 mol% NaCl and 14 mol% KCl

Couple	Melt	Temp. °C	E° dir	Reference (for "dir")	E° dep	Difference in E°
$H(I)/H_2$	a	135	1.202	[T]	1.22	- 0.02
Cu(I)/Cu(O)	b	135	0.745	[1,2]	0.79	- 0.045
Ag(I)/Ag(O)	b	150	0.839	[31,32]	0.83	+ 0.01
Ag(I)/Ag(O)	b	135	0.802	[1,2]	0.83	- 0.03
Hg(I)/Hg(O)	b	150	1.077	[31,32]	1.00	+ 0.08
Zn(II)/Zn(O)	b	150	0.304	[31,32]	0.32	- 0.02
Zn(II)/Zn(O)	a	135	0.287	[T]	0.32	- 0.03
Cd(II)/Cd(O)	b	150	0.387	[31]	0.44	- 0.05
Fe(II)/Fe(O)	a	135	0.652	[T]	0.55	+ 0.10
Co(II)/Co(O)	b	135	0.827	[T]	0.77	+ 0.06
Ni(II)/Ni(O)	a	135	0.927	[T]	0.88	+ 0.05

[T] result obtained in this thesis
dir from direct potential measurements
dep from deposition potentials, melt "b", ref. [82], 156°C

of 12.2 mV in the equilibrium potential of a M(II) / M(O) couple. Table III shows that the potentials actually found were 50 - 100 mV higher than predicted, while the increase in concentration of M^{2+} due to corrosion was definitely less than twofold. The discrepancy between predicted and found values of potentials also cannot be related to the slight difference in melt composition between [82] and this thesis. The expected change of potential caused by this difference in composition would be less than 10 mV [9]. It would, of course, involve the aluminum reference electrode and not the working metal electrode.

2. Coulometric Oxidation of Iron, Cobalt and Nickel

The required concentration of transition metal ions was produced in situ by coulometric oxidation of anodes of these metals. This technique, generally in use in molten salt systems, was successfully used by Hames and Plambeck [31,32], as well as Anders and Plambeck [1,2] for a number of elements in chloroaluminate melts; it allows the concentration to be changed without opening the cell. When cobalt was anodically dissolved into the melt, a deep blue color was observed in agreement with the spectrophotometric measurements of Øye and Gruen [62]. No such intense coloration was observed with iron or nickel.

The current efficiency of electrochemical oxidation was checked, in the case of iron, by subsequent

spectrophotometric analysis. After a correction was made for spontaneous corrosion (from a blank not subjected to coulometric oxidation) the data, shown in Table IV, indicate an efficiency of (96.8 ± 4.5)%.

A similar check of the coulometric reduction, which according to Hames and Plambeck [32] should have close to 100% efficiency for the zinc and mercury systems, revealed that in the case of iron (II) the efficiency of coulometric reduction varies with concentration and can be substantially less than 100%.

Current densities of 1.5 - 5.0 mA/cm^2 were used in the coulometric oxidations; they were close to the lower limit of current density available from the Model IV Coulometric Source. It took typically 35 min. to generate 0.1 milli-mole of M(II) ions. The polarization voltage varied widely between about 1.8V and 1.2V (0.9 V for iron). Care was taken to avoid higher polarization voltages that might cause some chlorine evolution. For this reason higher current densities were not used. It should be noted that the polarizing voltage often was more positive (anodic) than the standard potential of the H(I) / H_2 couple; this could not be avoided in our experimental set-up.

3. Drifting Potentials and Corrosion

As pointed out by Anders [1] certain drifting potentials have been found by all workers who made potential

Table IV

Coulometric Anodization of Iron

Amount of iron(II) generated, m moles	Amount corrected for corrosion, m moles	Amount of iron in the melt found by spectrophotometry m moles
0.150	0.26	0.27
0.250	0.36	0.34
0.250	0.36	0.33
0.300	0.41	0.40
0.500	0.61	0.59
0.250[a]	0.36	0.57

a. In this experiment 0.350 millimoles of iron(II) were generated and 0.100 millimoles were supposed to be removed by coulometric reduction

measurements in chloroaluminate melts [31,59]. Usually an explanation of these drifts was given in terms of slow chemical equilibria, typically involving polyatomic ions like the subvalent cadmium species in the studies of Munday and Corbett [59] or the Ag_m^{n+} ions postulated by Anders [1]. Drifting potentials have often been observed by one author in systems considered well-behaved by others.

The Zn(II) / Zn(O) electrode potentials may serve as an example; while Hames and Plambeck [31,32] found the couple well-behaved, Munday [58] and Anders [1] observed drifting potentials when zinc ions were generated in the melt by coulometric oxidation. In this thesis, Zn(II) / Zn(O) potentials were found to be stable for hours within 1 mV in agreement with [31,32]. When the coulometric generation of zinc ions was interrupted, there was of course a fall in the electrode potential due to the levelling of concentration within the electrode compartment. This lasted several minutes if the system was left resting; mechanical stirring reduced this interval to approximately one minute. After that, there was no significant change in the electrode potential with time.

The behavior of iron, cobalt and nickel electrodes was entirely different. After the initial decrease due to concentration levelling, the potential of these electrodes slowly drifted upwards as can be seen from typical examples

shown in Figure 4; iron showed the strongest drift of the three metals.

This, together with the large discrepancy between standard potential values obtained for the Fe (II) / Fe (0) couple by direct equilibrium potential measurements and those obtained from deposition potentials, led us to examine more closely the circumstances in which the potential of an iron electrode was drifting. Dependence of the drift magnitude on the concentration of iron (II) and on the previous history of the system (oxidation or reduction prior to potential measurements) was studied.

In these experiments, coulometric generation of iron (II) proceeded in steps of 100 μeq. After each generation period the equilibrium potential was followed for several hours. The concentration levelling was responsible for a potential decrease, which might be felt during the first minutes after the end of the coulometric generation. If the melt is shaken for a few seconds, this period is reduced to two to three minutes at maximum. An increase (upward drift) of the equilibrium potential follows; the magnitude of this drift decreases with time, but it is not a clear-cut exponential fall-off; there is rather a sudden easing of the drift after 30 - 35 minutes. When the equilibrium potentials were plotted against the logarithm of elapsed time (see Figure 5), two linear segments emerged,

Figure 4

Potential Drift of the Iron Electrode

The initial downward drift is probably due to concentration levelling. Compartment B was agitated slightly at "0" time, immediately after the interruption of the electrolytic current by which iron (II) had been generated in the compartment; compartment A was not agitated. An acceptable equilibrium value (stable to ± 1 mV for 10 minutes) would be obtained on both curves A and B after approximately 30 minutes.

Potential is increasing upwards in this Figure.

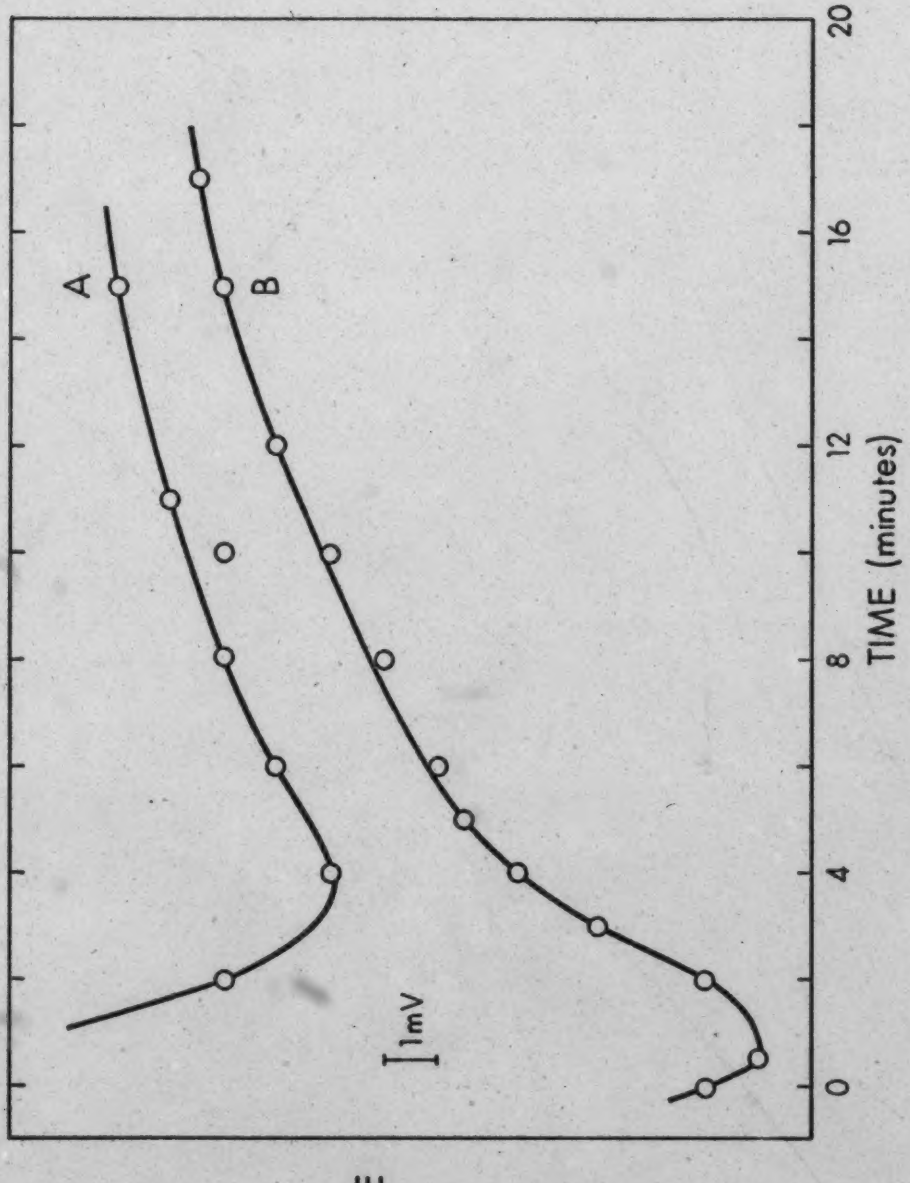
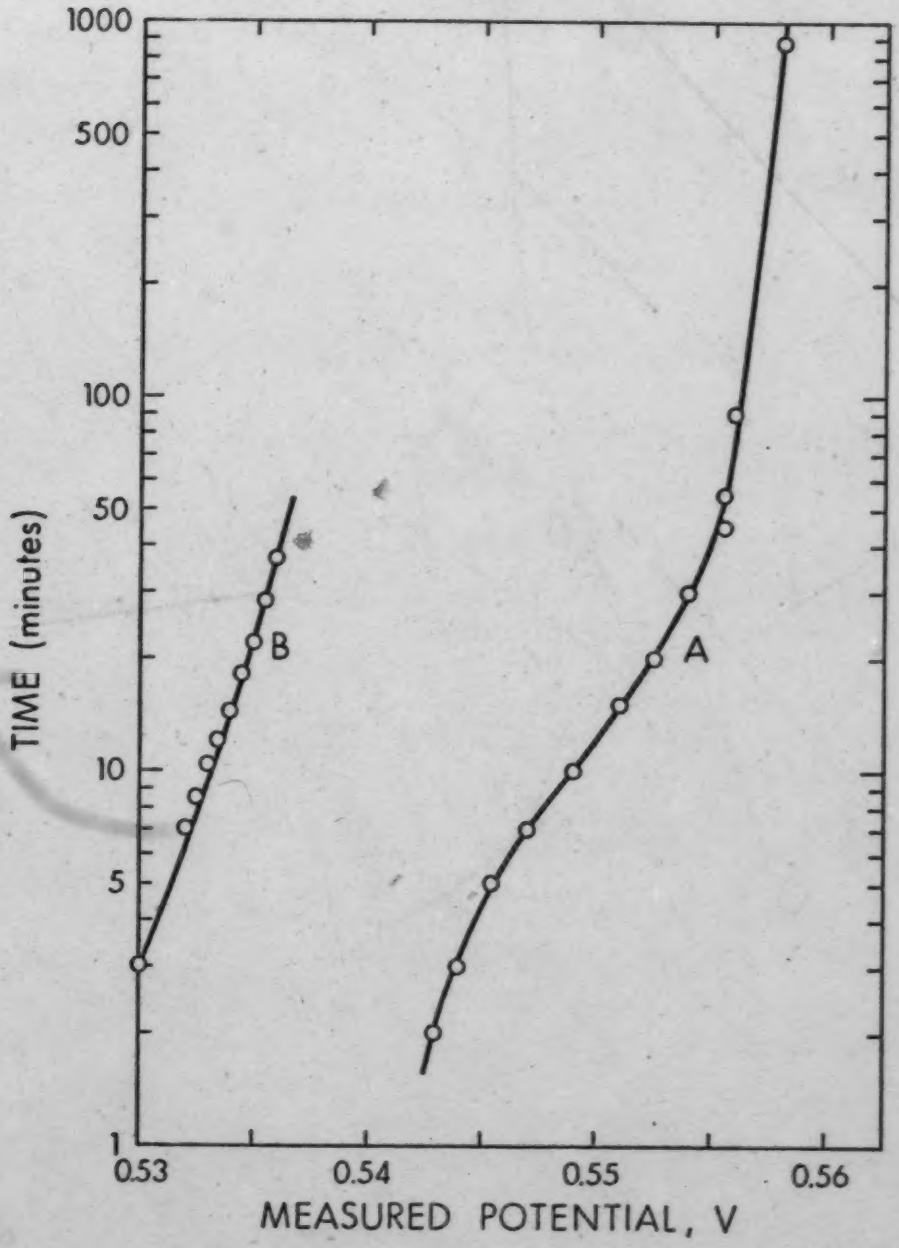

A
B
E
1mV
0
4
8
12
16
20
TIME (minutes)

Figure 5

Long-Term Potential Drift of the Iron Electrode

Curve A: points recorded after a coulometric oxidation of the iron electrode.

Curve B: points recorded after coulometric reduction (plating) of iron from the melt on an iron electrode.


1000
500
100
50
10
5
1
TIME (minutes)
B
A
0.53
0.54
0.55
0.56
MEASURED POTENTIAL, V

with slopes about 12 mV/unit log time up to 30 - 35 minutes and 3 mV/ unit log time thereafter. This feature is independent of the overall concentration of Fe (II) in the melt (from 0.1 to 0.4 mol%). When the coulometric process was reversed and a charge corresponding to the reduction of 100 μeq of Fe (II) to iron metal was passed through the system, the subsequent upward drift of the electrode potential was still observed, but the 12 mV slope segment was absent and the potential values were 30 - 40 mV lower than for identical Fe (II) concentrations after the anodic dissolution of iron.

Anders [1] observed a downward drift in some measurements of the Ag(I) / Ag(O) couple and he assumed the existence of polyatomic silver ions. The drift, however, was absent at lower concentrations. In the case of iron, there is an upward drift that does not depend on concentration. One could attempt to explain this behavior by assuming a slow dissociation or reduction of some complex compounds of iron. It seems, however, more realistic to seek the cause of drifting potentials in the known corrosion properties of chloraluminate melts. As was stated in the introduction, Kogan and Rabovskii [43] observed a periodic loosening of iron films from an aluminum surface in melts containing aluminum trichloride. They concluded that this was due to corrosion and quoted the rate of corrosion of iron at 200°C

found by Groshev for a NaCl - $AlCl_3$ melt [28] : 3.27 g/m^2h.

In order to interpret properly the results of electrode potential measurements in this thesis it became necessary to confirm or reject experimentally the existence of corrosion in the systems under study. This led to the determination of the total amount of dissolved iron in samples of the melt by the dipyridyl spectophotometric method [57,72]. The variable amount of iron, introduced in each sample deliberately by coulometric oxidation, was subtracted from this. The results are shown in Table V. The average rate of corrosion found in five experiments was 0.39 ± 0.05 g Fe/m^2h, which is one order of magnitude less than Groshev's value, but about half an order of magnitude greater than the minimum corrosion rate value 0.08 g/m^2h found by Groshev [28] in the presence of metallic aluminum.

Samples of melt from compartments where coulometric reduction was alternated with oxidation seem to show a distinctly higher rate of corrosion. This, however, is probably an artifact, due to a less than 100% efficiency of the coulometric reduction. Accordingly, these data were omitted when the average corrosion rate was calculated (Table V).

Table V

Iron Introduced into the Melt by Spontaneous Corrosion*

Experiment and Compartment	Millimoles Fe	Milligrams Fe
1	0.32**	17.6**
2, A	0.09	5.0
2, B	0.10	5.5
2, C	0.12	6.6
3, A	0.11	6.0
3, B	0.12	6.6
Average	0.108±0.013	5.9±0.7
Average rate of corrosion:	0.39±0.05 g Fe/m^2h	

*60 hours of contact with an iron spiral (geometrical area 2.5 cm^2)

**Coulometric reduction was tried out in Experiment 1; data from this experiment are not included in average results.

In two of the samples, no coulometric oxidation of the iron electrodes took place. In one case, an electrode with a visibly oxide-covered surface was deliberately used. In another run, the electrode was covered tightly with teflon tape and thus insulated from the gas phase above the melt; in this way, loss of iron through chemical transport in the gas phase was excluded. None of this affected the corrosion rate significantly, indicating that a chemical dissolution of iron took place directly in the melt and that it involved the iron metal itself, not just a surface oxide layer.

Separate experiments proved that ferric oxide dissolves in the melt to some extent, but reproducibility of the results was too low to permit quantitative conclusions. This dissolution, like metal corrosion, is most probably due to the presence of hydrogen compounds.

4. Voltammetry of Iron, Cobalt and Nickel

Both cathodic and anodic voltammetric waves of the three metals can be observed with a stationary platinum microelectrode. As an analytical tool this method is useful for the detection of small amounts of these metals, as was explained in the experimental section, Chapter II.6.

For the study of the Fe (II) / Fe (0), Co (II) / Co (0) and Ni (II) / Ni (0) redox couples in fused chloroaluminates, it is interesting to note the form of these voltammetric waves and their location on the scale of

potentials. All three metal couples under discussion showed the same form of voltammetric waves. The cathodic waves were simple, peak-type curves, similar to the H (I) / H_2 curve shown as curve A in Figure 6; the peaks were usually sharper than those of the hydrogen system. The anodic waves presented, without exception, a shoulder prior to the main wave: this indicates some irreversibility of the charge-transfer reaction [87]: at a certain point during the anodic sweep, metal deposition on the microelectrode has ceased while anodic dissolution of the metal has not yet begun. In agreement with this interpretation, the shoulder was always observed close to the zero current line. Consequently the potential at the shoulder inflection point represents a valid, though not very precise, estimate of the equilibrium potential for the reaction

$$M^{2+} + 2\,e^{-} = M\ (solid)$$

at the local concentration of M^{2+} in the neighborhood of the electrode. It may be taken as a lower limit of the equilibrium potential, which relates to the bulk concentration $X_{M^{2+}}$. Table VI contains comparisons of measured shoulder potentials and equilibrium potentials for the given bulk concentrations of M^{2+}. These equilibrium potentials were calculated from the standard potential data given in Table II.

Table VI

Voltammetric Results compared with Potential Measurements*

	X_M^{2+} * 10^3	E_s'(V)	E_{eq}'(V)	$E_{eq}-E_s'$(V)
Iron	0.9	0.49	0.528	0.04
	1.8	0.50	0.540	0.04
	2.7	0.52	0.548	0.03
	3.6	0.50	0.553	0.05
	4.5	0.50_5	0.556	0.05
				Average 0.042±0.008
Cobalt	1.1	0.69	0.707	0.02
	2.2	0.69	0.719	0.03
	3.3	0.71	0.726	0.02
	4.4	0.70	0.731	0.03
	5.4	0.72	0.735	0.015
	5.5	0.70_5	0.735	0.03
	6.3	0.72	0.738	0.02
	6.6	0.71	0.739	0.03
	7.2	0.72	0.740	0.02
	7.7	0.71	0.741	0.03
				Average 0.024±0.006
Nickel	1.4	0.78_5	0.811	0.02_5
	2.3	0.81_5	0.820	0.00_5
	3.4	0.82	0.827	0.01
	4.1	0.80	0.830	0.03
	4.5	0.83	0.831	0.00
	5.6	0.82	0.836	0.02
	6.8	0.82	0.839	0.02
				Average 0.016±0.011

*Shoulder potential E_s on the anodic voltammetric waves compared with values of equilibrium potentials E_{eq} calculated from standard potentials in Table II for the given bulk concentrations X_M^{2+}.

Table VII

Deposition Potential from Cathodic Voltammetric Waves

		$X*10^3$	Deposition Potential, V
Iron	This thesis	1.8	0.42
		2.7	0.42
		3.6	0.45
		4.5	0.47
	Yntema, ref. [82]	10	0.47
Cobalt	This thesis	4.4	0.66
		5.4	0.66
		5.5	0.67
		6.3	0.67
		6.6	0.67
		7.2	0.68
		7.7	0.68
	Yntema, ref. [82]	10	0.69
Nickel	This thesis	2.3	0.80
		3.4	0.80
		4.1	0.80
		4.5	0.81
		5.6	0.81_5
		6.8	0.80_5
	Yntema, ref. [82]	10	0.80

Estimates of deposition potentials may be obtained from voltammetric curves by extrapolating the rising portion of the cathodic wave to its intersection with the zero current line. These extrapolated values fit rather well with the deposition potentials determined by Verdieck and Yntema [82,83], as can be seen from Table VII. There is a significant difference, about 60 mV for iron, 40 mV for cobalt and 15 mV for nickel, between the shoulder and deposition potentials. In other words, potentials more cathodic than the equilibrium potentials are needed to initiate metal deposition: the charge-transfer reaction is at least slightly irreversible. The precision of voltammetric potential determinations, which is in the order of ± 10 mV, is too low to permit a quantitative assessment of this irreversibility. It can be stated that the Ni (II) / Ni (0) couple is somewhat less irreversible than the other two, in agreement with the findings of Martin de Fremont and co-workers [50].

The influence of corrosion on direct potential measurements is linked to the irreversibility of the system. An electrode which is being slowly oxidized and dissolved, cannot assume a potential more cathodic than that at which dissolution can proceed: this corrosion potential may be, and in an irreversible system necessarily is, more positive than the true equilibrium potential. If this is so, then

the potentials given in Table II are really corrosion potentials in the standard state or formal potentials relating to a slightly impure chloroaluminate melt. They constitute the upper limit of true standard potentials, while the lower limit is obtained from the shoulder potentials of anodic voltammetric waves. The two sets of limits compare as follows:

	Upper Limit, V	Lower Limit, V
Iron	0.652 ± 0.003	0.61 ± 0.01
Cobalt	0.827 ± 0.002	0.80 ± 0.01
Nickel	0.927 ± 0.003	0.91 ± 0.01

C. ELECTROCHEMISTRY OF THE HYDROGEN COUPLE

1. General Comments

As soon as it was ascertained that iron, cobalt and nickel are corroded in the melt, it became important to determine which component of the melt or impurity present in it was responsible for this corrosion. From the findings of Kochergin and Stolyarova [42] and from those of Martin de Fremont, Rosset and Leroy [50] we know that hydrogen compounds, if present in the melt, may be the prime cause of corrosion. These compounds are typically introduced into the melt during its preparation or handling in the form of traces of moisture. Trémillon and Letisse [46] found that traces of water, or hydrogen ions, react with the melt components and hydrogen chloride is formed. Martin de Fremont and co-workers [50] treat the corrosion phenomena as caused by hydrogen ions directly. Kochergin and Davydova [40], working in molten mixtures of chlorides and fluorides, suggest corrosion by non-volatile hydrogen compounds, probably hydroxides.

The study of the $H(I)/H_2$ couple in this thesis was begun with the assumption that the various hydrogen-containing species present in the melt are linked among themselves by rapid chemical equilibria and that whatever corrosive effect hydrogen compounds in the melt might show would be

proportional to the total hydrogen (I) concentration in the liquid phase.

2. Potentiometric Study of the Hydrogen Couple

It is known [46] that bare platinum metal can function as a hydrogen electrode in chloroaluminate melts when electroactive hydrogen compounds are present and the melt is saturated by hydrogen gas. In eutectic mixtures of molten hydroxides Goret [24] obtained similar voltammetric curves for the H_2O/H_2 redox system using either platinized or polished platinum electrodes. An analysis of these curves indicated that the exchange current of the $H(I)/H_2$ couple was large enough on bare platinum metal at 220°C to allow diffusion control of the oxidation or reduction current. Trémillon and Letisse [46] used a polished rotating platinum micro-electrode in molten sodium tetrachloroaluminate at 175°C.

In our experimental arrangement, hydrogen was brought in through a glass tube of 3 mm diameter and bubbled very slowly (about 1 ml/min.) through the melt; a spiral of 0.6 mm platinum wire was wound around the hydrogen inlet. The potential of this electrode was stable and its values well reproducible as long as the hydrogen flow was steady and the concentration of electroactive hydrogen compounds was sufficiently high. Concentrations greater than 2×10^{-3} mole fraction, as determined from voltammetric curves, were

required. At lower values of X_H, the potential readings were scattered; most often they were considerably higher than expected (about 150 mV more anodic), which would suggest that another electrochemical reaction began to control the electrode potential.

The standard potential E_H° was calculated from data recorded in Table VIII using the Nernst equation. The resulting value of 1.202 ± 0.005 V (see Table II) is an average of five single-point measurements. All experimental values taken at $X_H < 1.7 \times 10^{-3}$, as determined by voltammetry, were excluded from the calculations, because it could not be assumed that they were due only to the $H(I)/H_2$ redox system. Another, higher value for the standard potential of the hydrogen couple has also been included in Table II. It is an average of eight measurements, but it is considered less reliable because the melt was not completely saturated with hydrogen gas during that series of measurements. Some hydrogen was formed within the system, because the melt was in contact with metallic aluminum, but the activity of hydrogen did not reach the value corresponding to 1 atm. pressure over the melt and the difference between the two values of E_H° was 24 mV, significant at the 99.5% confidence level by t-test [45].

Verdieck and Yntema [82], by recording electrode potentials at given current densities and extrapolating to zero current, determined the deposition potentials of "H^+"

Table VIII

Hydrogen Electrode Potentials

Case A: Hydrogen pressure is 1 atm.:

Concentration of "HCl" determined voltammetrically, mol%	Measured E, V	Calculated E°, V
0.25	0.996	1.208
0.23	0.981	1.195
0.28	0.997	1.205
0.23	0.986	1.200
0.17	0.977	1.202
	Mean	1.202±0.005

Case B: Hydrogen pressure is the equilibrium pressure over a melt in contact with aluminum metal (compare [46]):

Concentration of "HCl" determined voltammetrically, mol%	Measured E, V	Calculated E°, V
0.66	1.055	1.232
1.14	1.064	1.222
0.90	1.064	1.230
0.30	1.011	1.216
1.42	1.080	1.230
1.09	1.070	1.229
0.74	1.052	1.221
	Mean	1.226±0.006

in a melt with $X_{H^+} = 0.01$ (added as H_2O). In their three-electrode arrangement which excluded the polarization of the reference electrode, a deposition potential is essentially the same as an equilibrium potential measured directly for a reversible couple. Using their value $E_{0.01} = 1.05$ V in the Nernst equation, at t = 156°C, we get $E^\circ_H = 1.22$ V, a value almost identical with the higher but less reliable value given in Table I of this thesis. That is understandable, because Verdieck and Yntema did not saturate their melt with hydrogen gas. The fact that HCl would be the electroactive species instead of H^+ [46] would in no way invalidate the numerical results. While Verdieck and Yntema admit some uncertainty in their X_{H^+} estimates, the logarithmic form of the Nernst equation dampens the size of the error in the resulting value of the standard potential.

3. Voltammetric Behavior of Hydrogen Compounds

There are very few references to the voltammetric behavior of the hydrogen couple in fused chloroaluminates. Its high redox potential excludes the use of mercury electrodes. Trémillon and Letisse [46] using a rotating platinum micro-electrode found a voltammetric wave corresponding to the reaction they write as:

$$2\ Al_2Cl_7^- + 2\ HCl + 2\ e^- \rightarrow 4\ AlCl_4^- + H_2.$$

In a NaCl - $AlCl_3$ melt with a pCl of 4.4, at 175°C, the wave

appears at a potential of about 1.35 V against a reference electrode of aluminum in a NaCl-saturated chloroaluminate melt. This would correspond to a potential of about 1.1 V between a hydrogen electrode in a near-eutectic chloroaluminate melt, as used in this thesis. (The potential of the aluminum reference electrode increases by 0.55 V between melts with 49.8 and 64 mol% $AlCl_3$, according to [9]; the potential of the hydrogen wave itself would increase by 0.28 V due to the change of 3.1 units in the pCl of the melt.) In fact, Torsi and Mamantov [78] have observed a wave at approximately 1.1 V whenever their melt (with 63 mol% $AlCl_3$) contained traces of moisture.

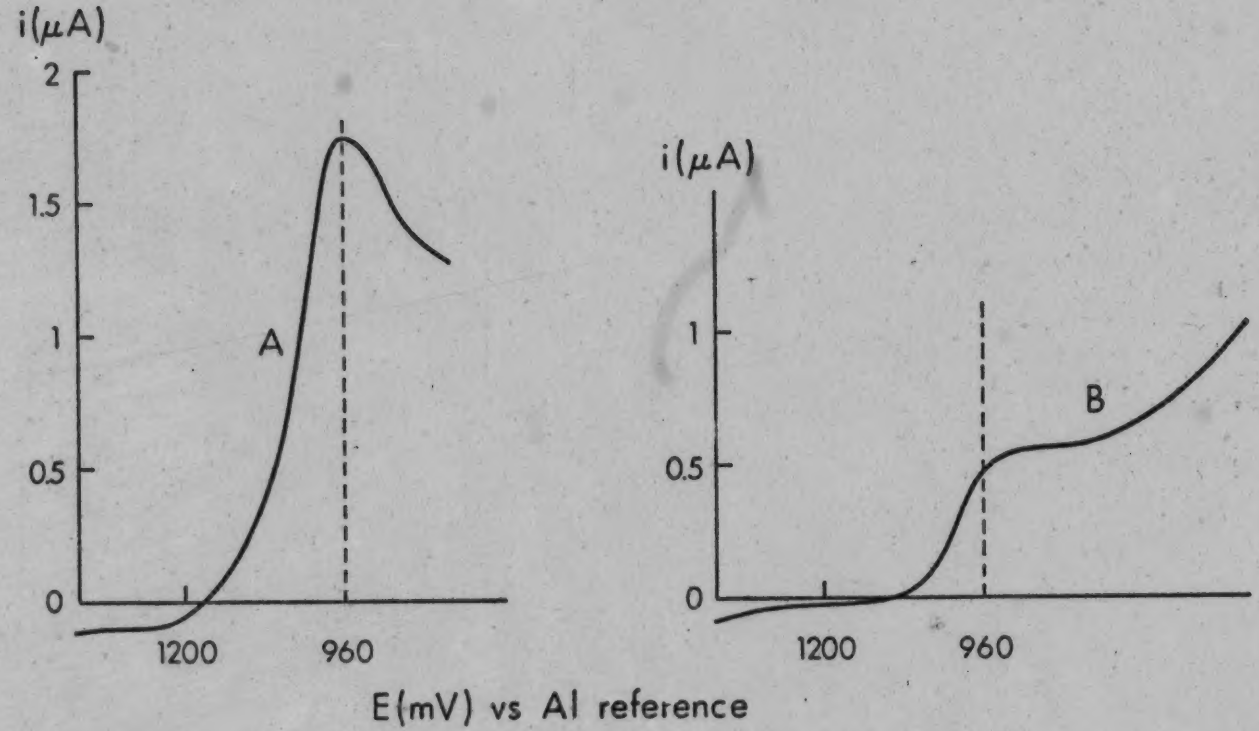
It was observed here that with a simple stationary platinum microelectrode a cathodic peak appeared at 960 ± 20 mV whenever hydrogen compounds were present (Fig. 6, curve A). This included moisture in the melt, water added in the form of crystalline salt hydrates, hydroxyl ions added as $Ba(OH)_2$ as well as gaseous HCl bubbled through the melt. The peak was similar in shape to those obtained for iron, cobalt and nickel. Peak behavior is expected in a diffusion-controlled system with a stationary electrode. As an anomaly, it should be noted that sometimes, typically in melts from which most of the hydrogen was eliminated by reduction, the peak failed to appear and linear voltammetric sweeps yielded waves somewhat similar to conventional polarographic ones (Fig. 6, curve B). The rising portion of

Figure 6

Cathodic Voltammetric Waves of Hydrogen (I)

Curve A: 0.12 mol% H(I); reducing agents can still lower this concentration

Curve B: 0.03 mol% H(I); steady state has been reached; reducing agents become ineffective


i(μA)
2
1.5
1
0.5
0
A
1200
960
i(μA)
1
0.5
0
B
1200
960
E(mV) vs Al reference

these waves stretched over an interval of 50 - 100 mV on the potential scale.

An anodic wave could also be observed, although this was somewhat less well defined than the corresponding waves of iron, cobalt and nickel, especially as far as the sharp drop in current corresponding to the termination of the anodic process was concerned.

In order to relate the height of the cathode peak to the concentration of hydrogen compounds in the melt, known amounts of water or hydroxyl ions were added to the molten system in the form of $BaCl_2.2\ H_2O$ crystals or solid anhydrous barium hydroxide, respectively. Cathodic voltammetric curves were recorded before and after these additions. Two or three voltammetric sweeps were usually made within ten minutes after each addition. This showed that a period of 5 - 10 minutes was needed for a batch of 50 - 100 mg of hydrogen-containing solid, in order to react fully with the melt and produce a maximum voltammetric effect. Only when this maximum peak height was attained, was the addition of hydrogen to the system assumed to be complete.

Cathodic currents were calculated from the heights of the voltammetric wave at the pre-selected value of E = 960 mV, which usually corresponded to the peak potential. Confining the readings to one value of the potential would permit some evaluation of the voltammetric response of the

system even when the form of the voltammetric wave was distorted with the peak being shifted towards more cathodic values or failing to appear altogether. Possible errors introduced by evaluating in this way curves like that of Fig. 6 B are not significant; grossly deformed voltammetric waves were not used in quantitative determinations.

Recording voltammograms prior to the additions of hydrogen compounds eliminates the immediate need for complete purification of the melt with respect to hydrogen--a task which proved to be very difficult under these experimental conditions, as will be discussed in the following subsection of this thesis. The method of voltammetric determination of hydrogen compounds, as used here, is then in fact one of standard additions. The reproducibility of this method is best illustrated by the numerical results, summarized in Table IX. Errors in single determinations are of the order of 10%, which is still acceptable for the calculation of electrode potentials: an error of ± 10% in the concentration determination corresponds to an uncertainty of ± 4 mV in the calculated value of the potential.

At concentrations of the order of 0.1 to 1 mol%, the increase in cathodic current at 960 mV was found to be proportional to the number of equivalents of hydrogen compounds brought into the melt; that is

$$i = 15 \pm 5 \ \mu A/\text{mol\% H},$$

Table IX

Voltammetric Determination of Hydrogen (as HCl)

A. Hydrogen added as $BaCl_2.2\ H_2O$:

$BaCl_2.2\ H_2O$ added, mg.	$10^3\ X_{HCl}$ calculated	Wave Height at 960 mV; μA	$10^3\ X_{HCl}$
68	0.82	1.4	0.83
125	1.50	2.1	1.2
195	2.35	4.1	2.4
282	3.39	5.2	3.1
345	4.15	7.0	4.15[a]

B. Hydrogen added as anhydrous $Ba(OH)_2$:

$Ba(OH)_2$ added, mg.	$10^3\ X_{HCl}$ calculated	Wave Height at 960 mV; μA	$10^3\ X_{HCl}$
211	2.80	3.2	3.2
466	6.19	6.0	6.0
565	7.50	8.6	8.7
773	10.26	10.2	10.26[a]

C. Hydrogen added in alternation as $BaCl_2.2\ H_2O$ or $Ba(OH)_2$:

$BaCl_2.2\ H_2O$ added, mg.	$Ba(OH)_2$ added mg.	$10^3\ X_{HCl}$ calculated	Wave Ht. at 960 mV; μA	$10^3\ X_{HCl}$ found
73	0	0.83	1.2	0.60
73	88	1.54	2.8	1.4
141	88	2.31	4.1	2.0
141	182	3.07	6.0	3.0
212	182	3.87	7.8	3.87[a]

a. preset value used for calibration
Total amount of melt: A:1.36 moles; B:0.88 moles; C:1.45 moles;
Calibration: μA/10^{-3} mole fraction 1.686 0.994 2.015

where the chemical symbol H is used to denote all hydrogen in the + 1 oxidation state. With the constant area of the microelectrode 0.003 cm^2 taken into account, the current density is

$$i/A = 5.0 \pm 1.7 \text{ mA/cm}^2 \text{ mol\% H.}$$

This value is high enough to fully account for the observed rate of corrosion of iron.

4. Purification of the Melt

As was mentioned in the experimental section, routine purification of the melt was accomplished by immersion of an aluminum spiral for three hours as suggested by Martin de Fremont and co-workers [50] and by Anders [1]. As far as the elimination of heavy metals was concerned, this procedure proved entirely satisfactory. No iron could be detected by the α, α'-dipyridyl spectrophotometric method [57] in the purified melt. The residual amount of iron must therefore have been less than 0.02 millimoles in about 0.1 mole of melt, i.e., $X_{Fe} \leq 2 \times 10^{-4}$. Voltammetric checks, too, showed no iron present, the limit of detection (see experimental section) being $X_{Fe} = 10^{-4}$ and even 10^{-5} using the anodic stripping technique. Voltammetric checks also confirmed the elimination of small amounts of nickel by the

same procedure.

The voltammetric wave of hydrogen, however, could never be completely suppressed by exposing the melt to metallic aluminum. Even after contact with aluminum metal for several days some hydrogen compounds were still present. If the initial H(I) concentration was about 1 mol%, it would readily be cut down to the order of 0.1 mol% (determined by voltammetry) during the first four hours, but there the purification process seemed to stop. Replacing the "used" aluminum surface, which was often covered by a blackish deposit, by a clean new one did not further reduce the voltammetric waves. When a negative enough potential was impressed on the aluminum electrode, the melt started to decompose and aluminum metal was deposited; meanwhile the hydrogen content seemed unchanged.

As it was thought that passivation of the aluminum metal might be inhibiting the reduction of hydrogen compounds, the cathodic ($H^+ \rightarrow H_2$) and anodic ($Al \rightarrow Al^{3+}$) processes were separated by having immersed in the melt both an aluminum and either an iron or a nickel electrode (area: 24 cm^2). The two were connected through an external circuit. This amounted to using electrolysis without an external power source, or internal electrolysis. The aluminum electrode could not be considered passive, because whenever it was reconnected through the external circuit to the iron or nickel cathode, an increased current was observed.

Periodic checks on the potential of the iron or nickel electrode with the circuit disconnected showed that the electrode process there continued: the potential was rising spontaneously towards the equilibrium, or steady-state corrosion, values found earlier for the Fe(II)/Fe(0) or Ni(II)/Ni(0) systems. The potential rise was slow and could last several hours. (An addition of water, as $BaCl_2.2\ H_2O$, provoked an almost instantaneous rise of the potential and in a few minutes, voltammograms would show the presence of metal ions due to corrosion.)

It is difficult, from these observations alone, to discard the possibility of one particular kind of passivation of the aluminum electrode, which was described by Holleck and Giner [35] and is due to the solubility of aluminum (III) chloride in the molten system being exceeded in the immediate vicinity of an aluminum anode. In such a case a layer of solid $AlCl_3$ would cover the aluminum anode and sever its contact with the liquid phase. Such a passivating layer would tend to disappear by dissolving in the melt spontaneously whenever the anodic reaction stopped (i.e., on each interruption of the external circuit).

The passivation phenomenon described by Holleck [35] is, however, strongly temperature-dependent as a result of the particular form of the NaCl (or KCl) - $AlCl_3$ phase diagram. If this phenomenon was responsible for the decrease of the electrolysis current, the effect should be less pronounced

at higher temperatures. In one experiment, the internal electrolysis was therefore carried out at 155°C, that is 20°C above the usual temperature. No improvement in the efficiency of the process could be observed. It was then concluded that passivation was not the limiting factor either in the electrolysis or in the simple reduction of hydrogen compounds in the melt by metallic aluminum.

After 4 - 5 hours of internal electrolysis a steady current of 1 - 3 mA (current density 0.08 - 0.25 mA/cm^2) was reached every time. The concentration of hydrogen compounds, determined from the voltammetric curves, also remained steady: $X_H = 3x10^{-4} - 10^{-3}$ (i.e., 0.03 - 0.1 mol%). In one experiment, values of $(1.0 \pm 0.2)x10^{-3}$ were obtained for three consecutive times, having added H_2O or OH^- and then electrolyzed.

In view of the high volatility of aluminum trichloride, the bubbling of an inert gas through the melt as suggested by Trémillon and Letisse [46] was not considered a promising method of purification. According to Fannin, King and Seegmiller [18] the melt formally composed of 64 mol% $AlCl_3$ and 36 mol% NaCl contains about 5 mol% Al_2Cl_6 (real equilibrium concentration at 175°C) while at formally 50 mol% $AlCl_3$ the true concentration of Al_2Cl_6 is negligible, below 10^{-4} mol%. The volatility would increase with increasing $X_{Al_2Cl_6}$.

Nevertheless, inert-gas bubbling for brief periods

of time (approximately 1 minute) was carried out. Both hydrogen and nitrogen were used with similar results: the concentration of hydrogen compounds in the melt decreased to about 5×10^{-3} mol% (i.e., below the detection limit). This, however, proved to be only a temporary effect and the concentration of hydrogen compounds increased spontaneously to levels between 0.01 and 0.1 mol% within about 30 minutes.

Summarizing all the observation of the purification process, it appears that there is within our system a source of an electroactive hydrogen-containing species, which could be solvated hydrogen ions or undissociated HCl. (The arguments of Trémillon and Letisse [46] in favor of HCl apply to molten $NaAlCl_4$ and do not exclude the presence of hydrogen ions in $AlCl_3$-rich melts.) This source maintains a steady-state concentration of hydrogen compounds, which is estimated from voltammetric curves to be between 0.03 and 0.1 mol%. The following possibilities must be considered:

A. The source is external to the melt. There could be some HCl in the dry-box atmosphere, in equilibrium with the HCl dissolved in the melt. It is less probable that small amounts of oxygen in the atmosphere would react with the melt or with the hydrogen which is produced by electrolysis on metallic cathodes.

B. The source is linked to impurities within the melt; this would imply that there is in the melt a larger concentration of hydrogen compounds with only a fraction of them being electroactive. One can think here of aluminum

complexes containing hydrogen and oxygen, formed through the contact of the melt with moisture, or of some organic impurities, which are known to be difficult to eliminate from commercial aluminum trichloride.

C. The steady state concentration of hydrogen-containing species is maintained by chemical equilibria involving the basic components of the melt.

All these possibilities will in turn be discussed.

5. Kinetics of Reduction of the Hydrogen Compounds in the Melt

The progress of the elimination of hydrogen compounds from the melt can be followed both by voltammetry and by direct potential measurements. During the internal electrolysis described above, the potential of the platinum spiral serving as hydrogen electrode decreased linearly with time, until the concentration of hydrogen compounds in the melt became too low ($X_H < 2 \times 10^{-3}$) to impress the equilibrium potential of the reaction

$$H^+ + e^- = 1/2\ H_2$$

upon the platinum electrode. A reaction formally obeying first-order kinetics would produce such a linear decrease of potential with time:

$$- dX = k\ X\ dt$$

$$- d\ \ln X = k\ dt$$

and as the differential form of the Nernst equation gives (with the pressure of hydrogen gas being constant)

$$dE = (RT/nF)\ d\ \ln X$$

one may write

$$-dE = (RT/nF)\ k\ dt.$$

The value of k (in sec^{-1}) at 135°C, is given by the following expression, with E in mV,

$$k = -0.028\ dE/dt.$$

Although the electrochemical reaction here necessarily has to be heterogeneous, it may by adequately described by formal first-order kinetics. For such a reaction we may calculate the rate constant k and then, by choosing one value of X_H, predict the rate of consumption of the electroactive species:

$$-dX/dt = k\ X_H$$

Working with one mole of melt and assuming 100% current efficiency, we can even predict the electrolysis current at that particular moment:

$$i = dQ/dt = -nFdN/dt = -nFdX/dt$$

where F is the Faraday and N is the number of moles of the electroactive species; note that N = X, because we have just

one mole of melt, and that the electrode reaction involves a transfer of one electron making n = 1, whether hydrogen ions or HCl are being reduced.

From the experimental data, shown in Figure 7, one gets $k = 1.9 \times 10^{-4}$ sec^{-1}; taking the lowest value of X_H at which the graph of Figure 7 is still linear, $X_H = 2 \times 10^{-3}$, a current of 38 mA is predicted. The current observed during the internal electrolysis was much less than this, 5 mA.

If the corrosion of iron were explainable entirely on the basis of the reaction with hydrogen compounds, the rate of iron corrosion should be the same as that of hydrogen compounds reduction in terms of electrochemical equivalents; in terms of moles, the rate of disappearance of hydrogen (I) should be twice the rate of appearance of iron (II). A current of 38 mA corresponds to a rate of iron corrosion of 2.0×10^{-7} moles $sec^{-1}/24$ cm^2 which is 0.30 moles/m^2h or 16 g Fe/m^2h for a hydrogen concentration $X_H = 2 \times 10^{-3}$. At the lowest concentration obtainable, $X_H = 3 \times 10^{-4}$, the corrosion rate would be 2.5 g Fe/m^2h for a current of 38 mA, but at the observed current of 5 mA it would be 0.33 g Fe/m^2h. This last number is in excellent agreement with the observed corrosion rate of (0.39 ± 0.05) g Fe/m^2h given in Table V.

When comparing the calculated and observed current, it should be kept in mind that during the internal electrolysis there is an aluminum plate in contact with the

melt and some hydrogen compounds may be chemically reduced by aluminum. The current corresponding to this direct reduction would not be present in the external circuit. But if we analyze the experimental set-up used, in which the areas of the aluminum and the iron plate were equal and the resistance in the external circuit between them only a few ohms, it becomes clear that one would have to assume the existence of a significantly greater hydrogen overpotential on iron than on aluminum, if a predominant fraction of the hydrogen compounds reduced were to be reduced on the aluminum plate. (The potentials of the iron and aluminum plate differed by less than 50 mV.) Assuming such an overpotential does not seem justified, because it is known that in aqueous solutions, hydrogen overpotentials on iron are low in comparison to overpotentials on other metals, e.g., zinc. Consequently, the discrepancy between calculated and observed currents related to the reduction of hydrogen compounds (38 mA and 5 mA in the example quoted above) is somewhat larger than can immediately be explained.

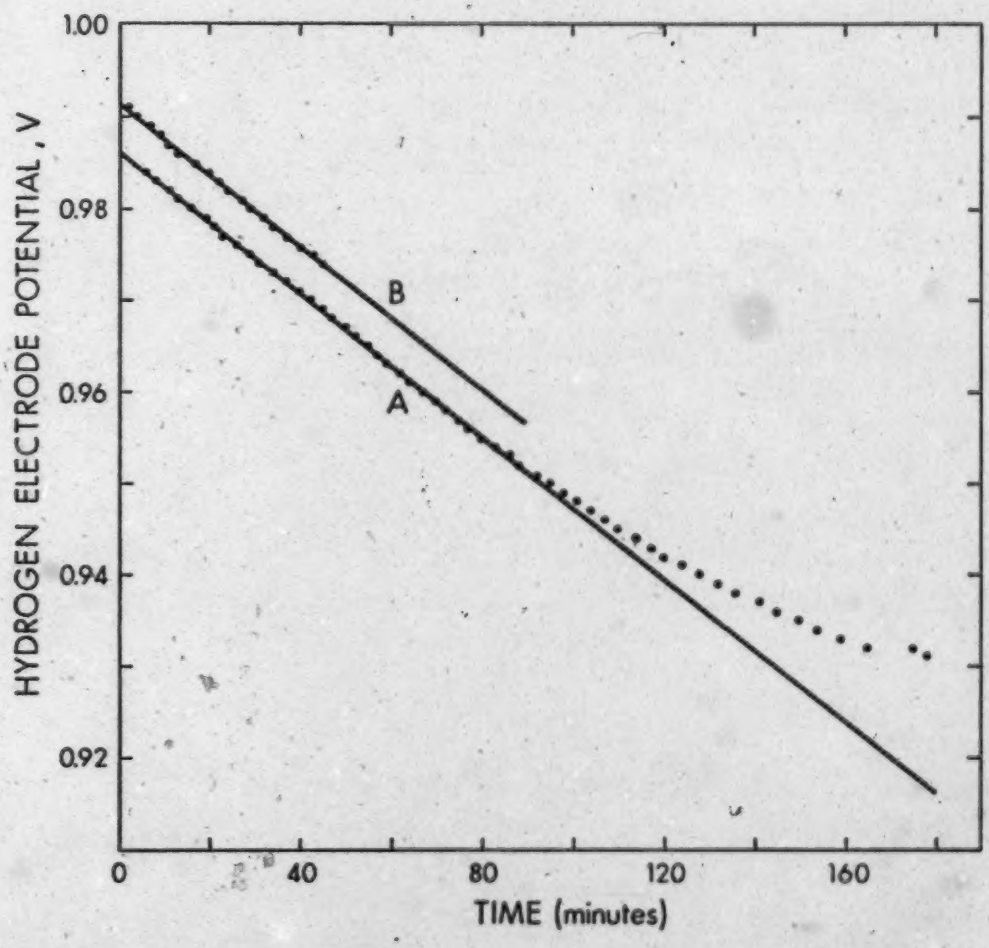
In comparing potentiometric and voltammetric data concerning the elimination of hydrogen compounds from the melt, we see that by the voltammetric method we can follow the process somewhat further. As was stated before, the

Figure 7

Kinetics of Hydrogen (I) Reduction

Lines A and B indicate two separate runs observed consecutively in the same compartment. Each time water has been added as $BaCl_2.2\ H_2O$ and is being eliminated by internal electrolysis. From the slopes of lines A and B the formal first-order rate constant is calculated to be

$k = 1.9 \times 10^{-4}\ sec^{-1}$


1.00
0.98
0.96
0.94
0.92
HYDROGEN ELECTRODE POTENTIAL, V
B
A
0
40
80
120
160
TIME (minutes)

platinum electrode ceases to respond properly to the $H(I)/H_2$ couple at about 0.2 mol% of hydrogen compounds in the melt. The reduction of these compounds, however, goes on and the "apparent equilibrium" concentration is established between 0.03 and 0.1 mol%.

The kinetic study allows us to estimate the time necessary for a conventional purification of the melt. From the above value of the pseudo first-order rate constant, the half-time of the reaction is calculated to be about one hour, indicating that more than three hours would be required to lower the hydrogen content by a factor of ten.

D. THE QUESTION OF MELT PURITY

1. Discussion of the Purification Process

It is clear from what was said in the introduction that different criteria have been used by various authors to assess the degree of purity of chloroaluminate melts, especially with respect to products of hydrolysis formed by the reaction between melt components and traces of moisture.

The voltammetric criterion used by Torsi and Mamantov [78] seems most reliable; from voltammetric curves reproduced in their paper one can estimate that these authors [77,78] used melts with less than 0.001 mol% H^+ (or HCl). These melts were either prepared from very pure aluminum and hydrogen chloride [5] or digested in sealed tubes with pieces of aluminum wire at 300°C for several days [77].

It is more difficult to say how pure were some of the melts prepared in less elaborate ways. Having studied the voltammetric behavior of hydrogen compounds, one can estimate from the current densities reported by Wade, Twellmeyer and Yntema [84] that their melts might have contained about 0.1 mol% H^+. Similar estimates would indicate that Trémillon and Letisse [46] had about 0.03 mol% HCl in their samples of molten $NaAlCl_4$ after nitrogen bubbling and less than 0.004 mol% HCl after bubbling combined with reduction by aluminum powder. There are some indications, however, that molten tetrachloroaluminates are easier to purify than $AlCl_3$-rich melts [50], which have a very low concentration of chloride ions.

In general, there seems to be a limiting concentration of hydrogen compounds which is relatively easy to reach. Difficulties arise when further purification is attempted. In our experiments this limit was approximately 0.1 mol% H. At higher concentrations, the reduction of hydrogen compounds by aluminum presented no difficulties. Voltammetric curves had the shape predicted by theory and the electrode process formally followed first-order kinetics. It is obviously only at these higher concentrations of hydrogen compounds that Martin de Fremont and co-workers [50] could observe the formation of hydrogen bubbles on the surface of aluminum wires immersed into the melt. Finally, as was mentioned earlier, Howie and Macmillan [37] found that a minimum

concentration of 0.2 mol% HCl was necessary to obtain smooth deposits of aluminum metal by electrolysis.

Below the limiting concentration the picture was different. Potentiometric data were no longer reliable and voltammetric peaks were shifted to more cathodic potentials. Current-voltage characteristics, recorded in a three-electrode arrangement, showed an erratic behavior. Their reproducibility was low, the current took one minute or even more to stabilize, and there was hysteresis, i.e., the currents depended not only on the potential actually imposed to the working electrode, but also on its previous potentials. In contrast to this, melts with more than 0.1 mol% H showed reproducible current-voltage characteristics conforming to Ohm's law, without hysteresis. Currents became stable within a few seonds after each adjustment of the working electrode potential.

All these results are compatible with the assumption stated above, that there is within the system a source of electroactive hydrogen compounds, which interferes with efforts to prepare hydrogen-free melts. When there is a higher concentration of electroactive hydrogen compounds in the melt already, this interference is not noticed.

2. Possible Sources of Melt Contamination

2.1 The Dry-Box Atmosphere

Contamination from this source is not very likely,

because the cell atmosphere is separated from the rest of the box by the fitted Teflon stopper. The box atmosphere consisted of dry nitrogen, passed through a molecular sieve and maintaining a slight overpressure inside the box. Two open dishes with phosphorus pentoxide were kept inside the box, providing an exposed geometrical surface of approximately 200 cm^2 of dessicant. If some humidity did enter the dry-box, either by diffusing through the large area of the rubber gloves [68] or at the beginning of an experiment, when equipment was being moved in and out, it would either be absorbed by the dessicant or react with some of the solid aluminum trichloride deposit on the box walls and be converted to hydrogen chloride.

A check on the presence of hydrogen chloride in the dry-box atmosphere was made under comparatively "adverse" conditions a short time after an experiment involving gaseous HCl had been carried out in the box. A trial analysis of 1.2 liters of the box atmosphere (24 hours contact with a standard carbonate solution and subsequent titration of the carbonate with HCl) showed the presence of not more than 1000 p.p.m. HCl. If Groshev's [27] solubility data are correct and applicable to the melt used here, then 100 times more HCl (a partial pressure of 0.1 atm) would be needed to maintain an equilibrium concentration of 0.03 mol% HCl in the melt, which was observed in this thesis.

2.2 Impurities in the Melt

After purification of the melt by protracted contact with aluminum metal, a steady-state concentration of hydrogen compounds of the order of 0.1 mol% remains. When internal electrolysis is applied, the residual current of about 3 mA would indicate a rate of reduction of hydrogen compounds of the order of 10^{-4} mole/hour; consequently the decrease in X_H ought to be measurable after 2-3 hours, if the hydrogen-containing electroactive species were not steadily regenerated. Moreover, as described above, when all hydrogen compounds were temporarily removed, they began reappearing after a few minutes. This might tentatively be explained in terms of a slow equilibrium within the melt, which ties the hydrogen-containing electroactive compound to other species present in the melt.

For the sake of simplicity, let us assume that the active compound is HCl, as was the case in the system studied by Trémillon and Letisse [46]. These authors found that hydrogen ions (and therefore indirectly water and hydroxyl ions as well) were quantitatively converted to hydrogen chloride. In the case of hydroxyl ions one could write

$$OH^- + Cl^- \rightarrow O^{2-} + HCl \qquad (R)$$

In the system studied by Tremillon and Letisse, X_{Cl^-} and X_{HCl} were practically of the same order of magnitude, 10^{-3},

while in the 64 mol% $AlCl_3$-melt X_{Cl^-} has a fixed value of about 3×10^{-8} [18] in contrast to $X_{HCl} > 10^{-4}$. It would not, therefore, be surprising, if the rate of reaction (R) was considerably slower under these conditions. It might in fact be comparable to the rate of the reverse reaction (R←), which would result in a slow chemical equilibrium. This is not incompatible with the assumption [46] that oxide ions react with the melt components

$$O^{2-} + Al_2Cl_7^- \rightarrow Al_2OCl_5^- + 2\ Cl^-, \qquad (S)$$

because one might assume that hydroxyl ions would react along similar lines and also form an aluminum-containing complex. It is then possible to speak about the general equilibrium

$$\underset{\text{free or complexed}}{(OH^-)} + Cl^- = \underset{\text{complexed}}{(O^{2-})} + HCl \qquad (R')$$

and define a constant K (including in it the factor X_{Cl^-}, whose value is fixed by the buffering action of the melt):

$$K = \frac{X_{O^{2-}} * X_{HCl}}{X_{OH^-}};$$

from this we obtain a mathematical relation between X_{HCl} and the overall mole fraction of hydrogen compounds

$$(h = X_{HCl} + X_{OH^-})$$

$$h = X_{HCl} * \left(1 + \frac{g}{X_{HCl} + K}\right),$$

where $g = X_{OH^-} + X_{O}2-$ is the overall mole fraction of oxygen compounds. At higher concentrations of hydrogen chloride, where $X_{HCl} > K$, the expression for h would simplify to

$$h = X_{HCl} + g$$

and one therefore finds $dh = dX_{HCl}$. In terms of chemical processes this means that any lowering of the overall H(I) concentration is done at the expense of HCl; no change in the concentration of hydrogen compounds other than HCl is involved and consequently it does not matter whether these compounds are fast or slow to react.

The situation changes in the case of $X_{HCl} < K$; the expression for h now simplifies to

$$h = X_{HCl} * (1 + g/K)$$

implying that under equilibrium conditions the overall change in H should now be larger than the change in X_{HCl}. If the formation of HCl according to reaction (R) or (R') is slow, it might at this point become the rate determining step in the whole process of hydrogen elimination.

If a hydrogen-containing organic impurity was present, it would probably form a carbonium ion [3,13], the influence of which could be formally described in the same way as that of hydroxyl ions. From an appropriate equation like

$$H\text{-}R^+ + Cl^- = R + HCl \qquad (R'')$$

one may again derive an equilibrium constant

$$K = \frac{X_R * X_{HCl}}{X_{HR^+}}$$

and obtain the same expression as above with g now standing for the overall mole fraction of organic compounds.

2.3 The Possibility of a Redox Cycle

A few words ought to be said about the hypothetical case that the steady-state hydrogen (I) concentration is linked not to other impurities, but to the basic components of the melt itself. This would occur if hydrogen gas could be oxidized by aluminum (III) or if hydrogen (I) could form a complex with a melt component, which would drastically lower the $H(I)/H_2$ redox potential.

Aluminum trichloride clearly cannot oxidize hydrogen gas while being itself reduced to the metal. The observation of Belyaev and Firsanova [4] indicates that even the reduction of aluminum (III) to aluminum (I) cannot be coupled with the oxidation of hydrogen into a spontaneous process; these authors have observed the reverse, oxidation of aluminum (I) by water. Thus aluminum (I) compounds, which according to Delimarskii [16] and Storozhenko [74] are present in the melt, would more probably be destroyed by HCl or H^+. This would also be in agreement with the findings of Howie and Macmillan [37].

Under normal conditions (reduction by aluminum metal or internal electrolysis) the cathodic reduction of hydrogen

compounds is coupled with the anodic dissolution of aluminum metal. Unless the latter was blocked by some kind of selective passivation, only reactions with sufficiently cathodic E°, that is, a negative E° on the aluminum scale, would provide an alternative oxidation process. In other words, complexation would have to shift the formal H^+/H_2 redox potential by more than 1 V, which is very improbable.

CHAPTER IV

CONCLUSIONS

Direct potential measurements in fused chloroaluminates are affected by impurities in the molten system. These impurities are very difficult to remove and one must assume that in all but some recent work in these melts, significant amounts of impurities were present during the measurements.

From the electrochemical point of view hydrogen compounds constitute the most active impurity. In fused chloroaluminates, the $H(I)/H_2$ couple has a higher redox potential than most metal-metal ion couples [50,82]. The standard potential of the $H(I)/H_2$ couple in a melt of 64 mol% $AlCl_3$, 22 mol% NaCl and 14 mol% KCl was determined in this thesis to be 1.202 ± 0.005 V against the Al(III)/Al(O) reference electrode in the same melt.

Under these circumstances reduction, either chemical or electrochemical, would seem to be the obvious way of removing hydrogen compounds from the melt and aluminum metal has been widely used as a chemical reducing agent. In order to study the kinetics of the reduction process, an internal electrolysis arrangement with an iron cathode was chosen. First-order kinetics were formally obeyed, with a rate

constant $k = 1.9 \times 10^{-4}$ sec^{-1}. The half-time was about one hour and consequently 3 - 4 hours were needed to lower the concentration of hydrogen compounds by a factor of ten.

Although there is no apparent thermodynamic reason that would predict a noticeably incomplete reduction of hydrogen compounds, all experiments in this work led to a steady state with a concentration of H(I), determined by voltammetry, being 0.1 mol% or slightly less. It is probable that this is caused by the interaction between the hydrogen redox couple and other impurities in the melt, either oxygen-containing or organic ones, both of which are difficult to eliminate.

The question, whether hydrogen is present as HCl, H^+, or in some other form, was not studied here. Trémillon and Letisse [46] found that H^+ was completely converted to HCl in an equimolar NaCl - $AlCl_3$ melt. This need not be quite so in near-eutectic melts, but results of potential measurements so far seem compatible with the assumption that a considerable fraction of H(I) is present as HCl even in these melts.

A quantitative study of the corrosion of iron in a melt with 64 mol% $AlCl_3$ was made. The average rate of corrosion was 0.39 ± 0.05 g Fe/m^2h. The corrosion of ferrous metals is thermodynamically impossible in pure molten chloroaluminates, but it may be easily accounted for by the presence of HCl. In the determination of standard electrode

potentials of iron, cobalt and nickel by direct potential measurements, corrosion was not extensive enough to invalidate measurements of metal ion concentrations. However, it may have interferred to some extent with the measurement of the equilibrium electrode potentials. The calculated values of standard potentials resulting from these experiments could then best be characterized as formal potentials at unit concentration in the given molten system. They are the higher limits of true standard potentials and may be complemented by lower limits, estimated from anodic voltammetric waves. The numerical results are as follows:

Couple	Direct Measurement or Higher Limit of E°	Lower Limit of E°
Fe(II) / Fe(0)	0.652 ± 0.003 V	0.61 ± 0.01 V
Co(II) / Co(0)	0.827 ± 0.002 V	0.80 ± 0.01 V
Ni(II) / Ni(0)	0.927 ± 0.003 V	0.91 ± 0.01 V

It is interesting to note that potential measurements on zinc electrodes indicate that zinc, although less noble than the three ferrous metals, is not corroded significantly. It is known from the work of Hames and Plambeck [32] that zinc (II) can be coulometrically reduced in the eutectic chloroaluminate melt with close to 100% efficiency. This was found not to be so in the case of iron.

BIBLIOGRAPHY

1. U. Anders: Ph. D. thesis. Univ. of Alberta, 1969.

2. U. Anders and J. A. Plambeck: Can J. Chem. 47, 3055-60, (1969).

3. R. A. Bailey and S. F. Prest: Can J. Chem. 49, 1-6, (1971).

4. A. I. Belyaev and L. A. Firsanova: "Monovalent Aluminum in Metallurgical Processes" [in Russian], Metallurgizdat, Moscow, 1959; quote in ref. [16].

5. N. J. Bjerrum, C. R. Boston and G. P. Smith: Inorg. Chem. 6, 1162-72, (1967).

6. N. J. Bjerrum, H. L. Davis and G. P. Smith: Inorg. Chem. 6, 1603-04, (1967).

7. N. J. Bjerrum and G. P. Smith: Inorg. Chem. 6, 1968-72, (1967).

8. C. R. Boston: "Molten Salt Chemistry of the Haloaluminates" in "Advances in Molten Salt Chemistry" (J. Braunstein, G. Mamantov and G. P. Smith, Editors), Vol. I, Plenum Press, New York, 1971; pages 129-63.

9. L. G. Boxall, H. L. Jones and R. A. Osteryoung: J. Electrochem. Soc. 120, 223-31, (1973)

10. G. Charlot and B Tremillon: "Chemical Reactions in Solvents and Melts", Pergamon Press, Toronto, 1969; page 504.

11. N. G. Chovnyk and M. V. Myshalov: Soviet Electrochemistry 6, 1583-86, (1970); Elektrokhimiya 6, 1659-62, (1970).

12. N. G. Chovnyk and M. S. Polyantseva: Soviet Electrochemistry 6, 1039-41, (1970); Elektrokhimiya 6, 1067-70, (1970).

13. J. H. R. Clarke and G. J. Hills: Chem. in Britain 9, 12-19, (1973).

14. J. D. Corbett: Inorg. Chem. 7, 198-208, (1968).

15. S. J. Cyvin, P. Klaeboe, E. Rytter and H. A. Øye: J. Chem. Phys. 52, 2776-78, (1970).

16. Yu. K. Delimarskii, V. F. Makogon and A. Ya Zhigailo: Soviet Electrochemistry 5, 98-100, (1969); Elektrokhimiya 5, 108-110, (1969).

17. F. R. Duke: J. Chem. Ed. 39, 57-58, (1962).

18. A. A. Fannin, Jr., L. A. King and D. W. Seegmiller: J. Electrochem. Soc. 119, 801-07, (1972).

19. A. A. Fannin, Jr., L. A. King and D. W. Seegmiller: Report SRL-TR-71-0018, USAF Academy, Colo. 80840, 1971.

20. C. G. Fink and D. N. Solanki: Trans. Electrochem. Soc. 91, 203-19, (1947).

21. W. Fischer and A. -L. Simon: Z. Anorg. Allgem. Chem. 306, 1-12, (1960).

22. M. Fleischmann and D. Pletcher: J. Electroanal. Chem. 25, 449-53, (1970).

23. H. Flood and T. Førland: Acta Chim. Scand. 1, 592-604, (1947).

24. J. Goret: Bull. Soc. Chim. France 1964, 1074-81.

25. G. L. Groshev: Tr. Khim. i Khim. Tekhnol. 1, 64-74, (1964); CA 61, 10303a.

26. G. L. Groshev: Tr. Khim. i Khim. Tekhnol. 1, 75-80, (1964); CA 61, 10302h.

27. G. L. Groshev: Khim. Prom. 46, 187-89, (1970).

28. G. L. Groshev: C. Sc. Thesis, Gorkii, USSR, 1966; quoted in ref. [43].

29. H. Grothe and C. A. Piel: Z. Elektrochem. 54, 210-15, (1950).

30. R. Gut: Helv. Chim. Acta 43, 830-42, (1960).

31. D. Hames: M. Sc. Thesis, Univ. of Alberta, 1968.

32. D. Hames and J. A. Plambeck: Can. J. Chem. 46, 1727-33, (1968).

33. M. Hansen: "Constitution of Binary Alloys", McGraw Hill, Toronto, 1958; pages 477, 661 and 828-29.

34. G. L. Holleck: J. Electrochem. Soc. 119, 1158-61, (1972).

35. G. L. Holleck and J. Giner: J. Electrochem. Soc. 119, 1161-66, (1972).

36. R. C. Howie and D. W. Macmillan: Inorg. Nucl. Chem. Letters 6, 399-401, (1970).

37. R. C. Howie and D. W. Macmillan: J. Appl. Electrochem. 2, 217-22, (1972).

38. H. L. Jones, L. G. Boxall and R. A. Osteryoung: J. Electroanal. Chem. 38, 476-78, (1972).

39. J. Kendall, E. D. Crittenden and H. K. Miller: J. Am. Chem. Soc. 45, 963-96, (1923).

40. V. P. Kochergin and V. G. Davydova: J. Appl. Chem. USSR 35, 1695-99, (1962).

41. V. P. Kochergin, M. S. Garpinenko, O. N. Skornyakova and M. Sh. Minullina: J. Appl. Chem. USSR 29, 621-25, (1956).

42. V. P. Kochergin and G. I. Stolyarova: J. Appl. Chem. USSR 29, 789-92, (1956).

43. V. M. Kogan and B. G. Rabovskii: Russ. J. Phys. Chem. 42, 864-67, (1968); Zh. Fiz. Khim. 42, 1650-54, (1968).

44. H. A. Laitinen: "Chemical Analysis", McGraw Hill, Toronto, 1960; pages 276-77.

45. H. A. Laitinen, same book, page 550.

46. G. Letisse and B. Trémillon: J. Electroanal. Chem. 17, 387-94, (1968).

47. H. Lux: Z. Elektrochem. 45, 303-09, (1939).

48. E. E. Marshall: Thesis, St. Louis University ,1938; quoted in ref. [49] and [82].

49. E. E. Marshall and L. F. Yntema: J. Phys. Chem. 46, 353-58, (1942).

50. R. Martin de Fremont, R. Rosset and M. Leroy: Bull. Soc. Chim. France 1964, 706-12.

51. J. W. Mellor: "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", Vol. II, Supplement III. Longmans, Green and Co., London, 1963; page 1673.

52. R. Midorikawa: J. Electrochem. Soc. Japan 23, 127-29, (1955).

53. R. Midorikawa: J. Electrochem. Soc. Japan 23, 352-55. (1955).

54. R. Midorikawa: J. Electrochem. Soc. Japan 24, 83-87, (1956).

55. R. Midorikawa: J. Electrochem. Soc. Japan 25, 13-16, (1957).

56. J. R. Morrey: Inorg. Chem. 2, 163-69, (1963).

57. M. L. Moss and M. G. Mellon: Anal. Chem. 14, 862-65, (1942)

58. T. C. F. Munday and J. D. Corbett: Inorg. Chem. 5, 1263-68, (1966).

59. T. C. F. Munday: Thesis. Diss. Abstr. 25, 6216, (1965).

60. T. Notoya: Electrochim. Acta 13, 2194-95, (1968).

61. R. M. Noyes: J. Chem. Ed. 40, 2-10, (1963).

62. H. A. Øye and D. M. Gruen: Inorg. Chem. 4, 1173-80, (1965).

63. P. Pascal: "Nouveau Traité de Chimie Minérale", Vol. II/2, Masson, Paris, 1963; page 120.

64. J. A. Plambeck: J. Chem. Eng. Data 12, 77-82, (1967).

65. V. A. Plotnikov, E. I. Kirichenko and N. S. Fortunatov: Zapiski Inst. Khim., Akad. Nauk Ukr. SSR 7, 159-72, (1940); CA 35, 3530.

66. V. A. Plotnikov and U. I. Shvartsman: Mem. Inst. Chem. Acad. Sci. Ukrain. SSR 3, 387-401, (1936); CA 31, 6093.

67. E. Rytter, H. A. Øye, S. J. Cyvin, B. N. Cyvin and P. Klaeboe: J. Inorg. Nucl. Chem. 35, 1185-98, (1973).

68. L. Šafařík and W. R. Heumann: Chem. Listy 66, 423-33, (1972).

69. K. Schulze and H. Hoff: Electrochim. Acta 17, 119-33, (1972).

70. R. P. Seward: J. Am. Chem. Soc. 67, 1189-91, (1945).

71. H. H. Sisler, C. A. VanderWerf and A. W. Davidson: "College Chemistry", 3rd. Edition, Macmillan, New York, 1967; pages 388 and 841.

72. F. D. Snell and C. T. Snell: "Colorimetric Methods of Analysis", Vol. II, 3rd. Edition, New York, 1949; pages 316-19.

73. Yu. I. Sorokin, Kh. L. Tseitlin, S. M. Babitskaya and L. V. Merzloukhova: Protection of Metals 5, 468-71, (1969); Zashch. Metal. 5, 536-40, (1969).

74. V. N. Storozhenko: Soviet Electrochem. 8, 942-45, (1972); Elektrokhimiya 8, 973-76, (1972).

75. J. Thonstad: Can. J. Chem. 42, 2739-43, (1964).

76. G. Torsi, K. W. Fung, G. M. Begun and G. Mamantov: Inorg. Chem. 10, 2285-90, (1971).

77. G. Torsi and G. Mamantov: Inorg. Chem. 10, 1900-02, (1971).

78. G. Torsi and G. Mamantov: J. Electroanal. Chem. 30, 193-201, (1971).

79. G. Torsi, G. Mamantov and G. M. Begun: Inorg. Nucl. Chem. Letters 6, 553-60, (1970).

80. W. D. Treadwell and L. Terebesi: Helv. Chim. Acta 18, 103-20, (1935).

81. B. Trémillon and G. Letisse: J. Electroanal. Chem. 17, 371-86, (1968).

82. R. G. Verdieck and L. F. Yntema: J. Phys. Chem. 46, 344-52, (1942).

83. R. G. Verdieck and L. F. Yntema: J. Phys. Chem. 48, 268-79, (1944).

84. W. H. Wade, G. O. Twellmeyer and L. F. Yntema: Trans. Electrochem. Soc. 78, 77-90, (1940).

85. L. Wasilewski, A. Kaczorowski and M. Dynkin: Przemysl Chem. 18, 608-17, (1934).

86. R. Wehrmann and L. F. Yntema: J. Phys. Chem. 48, 259-68, (1944).

87. L. Meites: "Polarographic Techniques", John Wiley, New York, 1965; page 581.

APPENDIX

Equilibrium Potentials of Iron

9g melt, 66 mol% $AlCl_3$

Generated meq Fe(II)	Mole Fraction of Fe(II)	E_{eq}	E° (calculated)
0.10	6.1×10^{-4}	0.534	0.664
0.20	1.2×10^{-3}	0.538	0.656
0.40	2.4×10^{-3}	0.546	0.652
0.60	3.7×10^{-3}	0.553	0.652
0.80	4.9×10^{-3}	0.557	0.651
1.00	6.1×10^{-3}	0.561	0.651
			0.651

5.8g melt, 66 mol% $AlCl_3$

0.10	9.4×10^{-4}	0.524	0.647
0.20	1.9×10^{-3}	0.530	0.641
0.30	2.8×10^{-3}	0.536	0.640
0.40	3.8×10^{-3}	0.540	0.638
0.50	4.7×10^{-3}	0.544	0.638
0.60	5.7×10^{-3}	0.548	0.639
0.70	6.6×10^{-3}	0.551	0.640
0.80	7.5×10^{-3}	0.557	0.643
1.00	9.4×10^{-3}	0.558	0.640
			0.640

Generated meq Fe(II)	Mole Fraction of Fe(II)	E_{eq}	E° (calculated)
	5.0g melt, 66 mol% $AlCl_3$		
0.10	1.1×10^{-3}	0.528	0.646
0.20	2.2×10^{-3}	0.537	0.643
0.30	3.3×10^{-3}	0.542	0.641
0.40	4.4×10^{-3}	0.548	0.642
0.50	5.5×10^{-3}	0.552	0.642
0.60	6.6×10^{-3}	0.556	0.643
0.70	7.7×10^{-3}	0.558	0.642
0.80	8.8×10^{-3}	0.561	0.643
1.00	1.1×10^{-2}	0.565	0.643
			0.642
	8.2g melt, 66 mol% $AlCl_3$		
0.40	2.7×10^{-3}	0.541	0.646
0.64	4.3×10^{-3}	0.548	0.644
1.00	6.6×10^{-3}	0.554	0.642
1.20	8.1×10^{-3}	0.558	0.643
			0.643
	7.5g melt, 66 mol% $AlCl_3$		
0.40	2.9×10^{-3}	0.547	0.650
0.60	4.4×10^{-3}	0.554	0.650
0.80	5.8×10^{-3}	0.558	0.649
1.00	7.3×10^{-3}	0.561	0.647
1.20	8.7×10^{-3}	0.566	0.649
			0.648

64 mol% $AlCl_3$

Weight of Melt, g	Amount of Fe (from spectrophotometry) m moles	Mole Fraction of Fe(II)	E_{eq}	E° (calculated)
11.4	0.57	5.4×10^{-3}	0.555	0.647
11.6	0.40	3.8×10^{-3}	0.553	0.651
11.9	0.59	5.4×10^{-3}	0.559	0.650
8.2	0.27	3.6×10^{-3}	0.547	0.651
6.9	0.13	2.1×10^{-3}	0.548	0.656
9.5	0.34	3.9×10^{-3}	0.557	0.655
9.1	0.33	3.9×10^{-3}	0.558	0.656

6g melt, 64 mol% $AlCl_3$

Generated meq Fe(II)	Mole Fraction of Fe(II)	E_{eq}	E° (calculated)
0.10	9.0×10^{-4}	0.536	0.660
0.20	1.8×10^{-3}	0.543	0.654
0.30	2.7×10^{-3}	0.546	0.650
0.40	3.6×10^{-3}	0.555	0.653
0.50	4.5×10^{-3}	0.558	0.652
			0.652

Equilibrium Potentials of Cobalt

7g melt, 66% $AlCl_3$

Generated meq Co(II)	Mole Fraction of Co(II)	E_{eq}	E° (calculated)
0.10	7.9×10^{-4}	0.715	0.841
0.14	1.1×10^{-3}	0.717	0.837
0.18	1.4×10^{-3}	0.719	0.835
0.24	1.9×10^{-3}	0.721	0.832
0.30	2.4×10^{-3}	0.723	0.830
0.40	3.1×10^{-3}	0.725	0.827
0.50	3.9×10^{-3}	0.729	0.827
0.60	4.7×10^{-3}	0.733	0.828
0.70	5.5×10^{-3}	0.736	0.828
0.80	6.3×10^{-3}	0.738	0.827
1.00	7.9×10^{-3}	0.742	0.828
			0.828

7g melt, 66% $AlCl_3$

0.10	7.9×10^{-4}	0.712	0.838
0.15	1.2×10^{-3}	0.715	0.834
0.20	1.6×10^{-3}	0.718	0.832
0.25	2.0×10^{-3}	0.722	0.832
0.30	2.4×10^{-3}	0.724	0.831
0.35	2.7×10^{-3}	0.724	0.828
0.40	3.1×10^{-3}	0.728	0.830
0.50	3.9×10^{-3}	0.730	0.828
0.60	4.7×10^{-3}	0.733	0.827
0.70	5.5×10^{-3}	0.735	0.827
0.80	6.3×10^{-3}	0.737	0.826
1.00	7.9×10^{-3}	0.740	0.826
			0.826

8g melt, 66 mol% $AlCl_3$

(Cobalt plated on platinum electrode)

Generated meq Co(II)	Mole Fraction of Co(II)	E_{eq}	E° (calculated)
0.10	6.8×10^{-4}	0.694	0.822
0.20	1.4×10^{-3}	0.704	0.820
0.30	2.1×10^{-3}	0.710	0.819
0.40	2.8×10^{-3}	0.716	0.820
0.50	3.4×10^{-3}	0.720	0.820
0.60	4.1×10^{-3}	0.722	0.819
0.80	5.5×10^{-3}	0.728	0.820
1.00	6.8×10^{-3}	0.732	0.820
			0.820

6.0 melt, 64 mol% $AlCl_3$, wire "2"

0.10	9.0×10^{-4}	0.739	0.863
0.15	1.4×10^{-3}	0.741	0.858
0.20	1.8×10^{-3}	0.744	0.855
0.35	3.2×10^{-3}	0.743	0.845
0.50	4.5×10^{-3}	0.752	0.847
0.70	6.3×10^{-3}	0.756	0.845
0.80	7.2×10^{-3}	0.756	0.843
1.00	9.0×10^{-3}	0.757	0.840
			0.843

4.9g melt, 64 mol% $AlCl_3$, wire "2"

Generated meq Co(II)	Mole Fraction of Co(II)	E_{eq}	E° (calculated)
0.10	1.1×10^{-3}	0.742	0.862
0.20	2.2×10^{-3}	0.742	0.850
0.30	3.3×10^{-3}	0.747	0.848
0.40	4.4×10^{-3}	0.746	0.842
0.50	5.5×10^{-3}	0.748	0.840
0.60	6.6×10^{-3}	0.750	0.838
0.70	7.7×10^{-3}	0.753	0.839
			0.839

6.6g melt, 66 mol% $AlCl_3$, wire "2"

0.10	8.2×10^{-4}	0.739	0.864
0.20	1.6×10^{-3}	0.737	0.850
0.30	2.4×10^{-3}	0.738	0.844
0.40	3.3×10^{-3}	0.740	0.841
0.50	4.1×10^{-3}	0.741	0.838
			0.839

Equilibrium Potentials of Nickel

Generated meq Ni(II)	Mole Fraction of Ni(II)	E_{eq}	E° (calculated)
	4.0g melt, 64 mol% $AlCl_3$		
0.04	5.4×10^{-4}	0.825	0.958
0.10	1.4×10^{-3}	0.833	0.946
0.20	2.7×10^{-3}	0.835	0.939
0.30	4.1×10^{-3}	0.837	0.934
0.40	5.4×10^{-3}	0.839	0.931
0.50	6.8×10^{-3}	0.840	0.928
			0.928
	4.8g melt, 66 mol% $AlCl_3$		
0.05	5.6×10^{-4}	0.809	0.941
0.10	1.1×10^{-3}	0.813	0.933
0.20	2.3×10^{-3}	0.820	0.927
0.30	3.4×10^{-3}	0.825	0.925
0.40	4.5×10^{-3}	0.830	0.925
0.50	5.6×10^{-3}	0.834	0.925
			0.925
	6.0g melt, 64 mol% $AlCl_3$		
0.10	9.1×10^{-4}	0.812	0.936
0.20	1.8×10^{-3}	0.819	0.930
0.30	2.7×10^{-3}	0.823	0.927
0.40	3.6×10^{-3}	0.825	0.924
0.50	4.5×10^{-3}	0.831	0.926
0.60	5.4×10^{-3}	0.833	0.925
0.80	7.2×10^{-3}	0.839	0.927
			0.926

8.2g melt, 66 mol% $AlCl_3$

Generated meq Ni(II)	Mole Fraction of Ni(II)	E_{eq}	E° (calculated)
0.20	1.3×10^{-3}	0.819	0.936
0.40	2.7×10^{-3}	0.830	0.934
0.61	4.1×10^{-3}	0.837	0.934
0.80	5.3×10^{-3}	0.840	0.932
1.00	6.7×10^{-3}	0.845	0.933
			0.933

5.8g melt, 66 mol% $AlCl_3$

0.20	1.9×10^{-3}	0.816	0.927
0.30	2.8×10^{-3}	0.822	0.926
0.40	3.8×10^{-3}	0.827	0.925
0.50	4.7×10^{-3}	0.831	0.925
0.60	5.7×10^{-3}	0.835	0.926
0.70	6.6×10^{-3}	0.837	0.925
0.80	7.6×10^{-3}	0.839	0.925
1.00	9.4×10^{-3}	0.842	0.924
1.20	1.13×10^{-2}	0.846	0.925
			0.925

Equilibrium Potentials of Zinc

11.2g melt, 64 mol% $AlCl_3$

Generated meq Zn(II)	Mole Fraction of Zn(II)	E_{eq}	E° (calculated)
0.10	4.9×10^{-4}	0.163	0.298
0.20	9.8×10^{-4}	0.171	0.293
0.30	1.5×10^{-3}	0.174	0.289
0.40	1.9×10^{-3}	0.177	0.287
0.50	2.4×10^{-3}	0.180	0.286
0.60	2.9×10^{-3}	0.185	0.288
0.70	3.4×10^{-3}	0.187	0.287
0.80	3.9×10^{-3}	0.190	0.288
0.90	4.4×10^{-3}	0.192	0.288
1.00	4.9×10^{-3}	0.194	0.288
1.10	5.3×10^{-3}	0.195	0.287
			0.287

Estimated 10g melt, 64 mol% $AlCl_3$

0.10	5.10^{-4}	0.170	0.30